

CHROMIUM, MOLYBDENUM AND TUNGSTENANNUAL SURVEY COVERING THE YEAR 1974

DONALD J. DARENSBOURG and MARCETTA YORK DARENSBOURG

Department of Chemistry, Tulane University, New Orleans,  
Louisiana 70118 (U.S.A.)CONTENTS

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### Introduction

There are slight changes in the CONTENTS arrangement of the Survey of 1974 literature from previous years; those include replacing the word "Preparative" with "Synthesis and Reactivity" and, under that division, a section on "Metal-metal bonded complexes" has been defined.

A few words of direction are in order for proper or complete use of this Survey. Since the principal tool for probing fluxionality of organometallic compounds is  $^1\text{H}$  or  $^{13}\text{C}$  nmr, mechanistic studies of that sort are in the nmr section under "Spectroscopic Studies." Similarly, the good deal of work that has been done with metal carbonyl derivatives as probes of ligand conformation is in general under nmr studies and will include the synthesis of several new ligands and complexes, precluding them from the "Synthesis and Reactivity: Lewis base derivatives" section.

We have covered the primary literature directly from the respective journals from January 1, 1974 to December 31, 1974. However some of the less available journals as well as all patents were covered from Chemical Abstracts. Doctoral dissertations are listed separately in this Survey and were reviewed by abstract only.

Finally, only the two most prevalent abbreviations will be given here. In general, we have used "Cp" to designate

$\pi$ -cyclopentadienyl,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>; and "dppe" to designate 1,2-bis-diphenylphosphinoethane, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>. All other abbreviations are hopefully described in the text.

### Dissertations

Studies involving the preparation of tungsten and molybdenum carbonyl complexes containing sulfur ligands, e.g., CpMo(CO)<sub>3</sub>SR, have been carried out by Watkins.<sup>1</sup> Derivatives of CpW(CO)<sub>3</sub> with Group IV elements were prepared in an investigation by Turnipseed.<sup>2</sup> The reactions of Cp<sub>2</sub>WH<sub>2</sub> and Cp<sub>2</sub>MoH<sub>2</sub> with dihalocarbene precursors have been examined by Chen,<sup>3</sup> whereas electrophilic additions to 2-alkenyl and 2-alkynyl-transition metal complexes including some of molybdenum have been studied by Lichtenberg.<sup>4</sup> The reactions of (C<sub>7</sub>H<sub>7</sub>)M(CO)<sub>2</sub>I (M = Mo, W) with Group Va ligands and M(CO)<sub>6</sub> (M = Cr, Mo, W) with bis(diphenylstibino)methane have been investigated by Beall.<sup>5</sup> Studies of the ligand properties of phosphonitrilic derivatives, including (N<sub>4</sub>P<sub>4</sub>Me<sub>9</sub><sup>+</sup>)(Cr(CO)<sub>5</sub>I<sup>-</sup>) and N<sub>4</sub>P<sub>4</sub>(NMe<sub>2</sub>)<sub>8</sub>W(CO)<sub>4</sub>, were part of a thesis by Calhoun.<sup>6</sup>

The reactions of MoCl<sub>5</sub> with Mo(CO)<sub>5</sub>Cl<sup>-</sup> have been studied by Delphin.<sup>7</sup> The reactivity and magnetochemistry of metallocenes, including (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cr, have been reported.<sup>8</sup> Chemical and structural studies of cyanide and isocyanide complexes of molybdenum is the subject of a thesis by Novotny.<sup>9</sup>

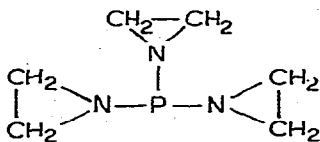
Hyde has reported infrared intensities and the kinetics of substitution reactions in substituted molybdenum and tungsten tetracarbonyl derivatives;<sup>10</sup> also infrared intensity studies of some tricarbonyl and dicarbonyl species of chromium

and molybdenum have been reported by Stanger.<sup>11</sup> The vibrational spectra of some transition metal organometallic complexes including (norbornadiene)M(CO)<sub>4</sub> (M = Cr, Mo, W) have been investigated by Barna.<sup>12</sup> Spectroscopic studies of metal-metal bonded systems including MM'(CO)<sub>10</sub><sup>-</sup> (M' = Cr, Mo, W; M = Mn, Re)<sup>13</sup> and other derivatives containing Cr-Cr and W-W bonds<sup>14</sup> have appeared.

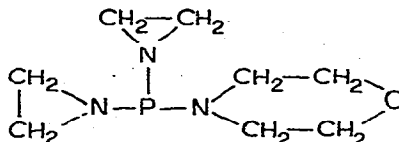
The application of X-ray photoelectron spectroscopy to the study of some organometallic compounds of molybdenum as well as some synthetic studies of molybdenum carbonyl phosphines have been carried out by Matienzo.<sup>15</sup> The X-ray structures of some novel transition-metal complexes including MoCl<sub>2</sub>(NO)<sub>2</sub>[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> and Mo<sub>2</sub>(CO)<sub>6</sub>[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PNH]<sub>3</sub>·1/2C<sub>4</sub>H<sub>8</sub>O have been determined by Visscher.<sup>16</sup>

### Synthesis and Reactivity

Lewis base derivatives of metal carbonyls. Numerous contributions involving the synthesis and characterization of substituted derivatives of metal carbonyls have appeared in the literature during this review period. The complexing properties of tris-(aziridino)phosphine (I) and bis-(aziridino)morpholinophosphine (II), groups of interest in cancer chemotherapy, were reported



(I)



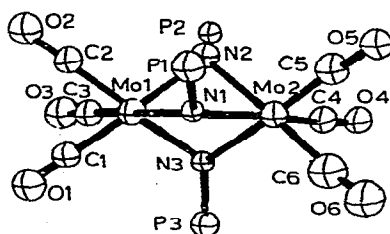
(II)

by R. B. King.<sup>17</sup> The binding site is through P in complexes such as IM(CO)<sub>5</sub> (M = Cr and/or Mo) and I<sub>2</sub>MCl<sub>2</sub> (M = Pd, Pt)

although the cis-trans geometry of the latter complex was not established. One of the complexes,  $(C_2H_4N)_2P(NC_4H_8O)Mo(CO)_5$ , displayed potential in preliminary screening (L-1210 lymphoid leukemia in BDF<sub>1</sub> mice) as a relatively non-toxic, anti-leukemia agent.

Phosphorus-bound dimethylaminodimethylphosphine derivatives of VIB carbonyls,  $M(CO)_5(PMe_2(NMe_2))$  furnish a route to  $M(CO)_5PMe_2Cl$  through reaction with HCl.<sup>18</sup> Reaction of 1,2,4,5- $Br_4C_6H_2$  with  $NaPPh_2$  in liquid  $NH_3$  has afforded a 55% yield of bis(diphenylphosphino)amine.<sup>19</sup> Further reaction of this ligand with  $Cr(CO)_6$  gave a good yield of  $Cr(CO)_4[(PPh_2)_2NH]$ .

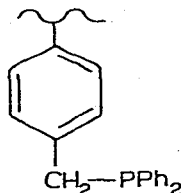
The previously formulated  $[Mo(CO)_2(\mu-CO)(Ph_3PNH)_2]_2$  complex has been shown to actually be  $Mo_2(CO)_6(\mu-Ph_3PNH)_3$  (III) in which local  $C_{3v}$  symmetry obtains for the  $Mo(CO)_3$  moieties and the phosphinimine ligands bridge the  $Mo(CO)_3$  centers in a unique phosphoniumamide, 4-electron donor manner  $(Ph_3P^+-N^--H)$ .<sup>20</sup> The present formulation is based on detailed chemical analyses, spectroscopic and single-crystal X-ray structure studies.



(III)

cis- $(F_3P:NPF_2)_2Mo(CO)_4$  has been prepared from (bicycloheptadiene) $Mo(CO)_4$  and  $F_3P:NPF_2$ .<sup>21</sup> This reaction was employed in the separation of  $F_3P:NPF_2$  from  $Me_3SiF$  during the preparation of  $F_3P:NPF_2$  from  $(Me_3Si)_2NPF_2$  and  $PF_5$ .

In an extensive publication dealing with the synthetic and catalytic studies of polymer-bound metal carbonyls, Pittman and co-workers have reported the first preparation of polymeric substitution products via the photochemical technique.<sup>22</sup> In this manner the Group VIb hexacarbonyls were reacted with the linear and cross-linked polymeric analogs of benzyldiphenylphosphine (IV) to yield both mono- and trans-disubstituted derivatives.

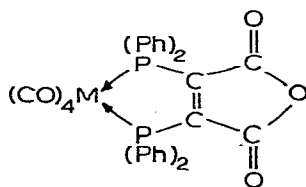


(IV)

Several chelating phosphine derivatives have been reported. These include complexes of the type  $M(CO)_4(L-L)$  and cis- $M(CO)_2(L-L)_2$  ( $M = Cr, Mo, W$ ; and  $L-L = 1,2$ -bis(diphenylphosphine)ethane, 1,2-bis(diphenylarsine)ethane, 1,4-bis(diphenylphosphine)butane, and 1,4-bis(diphenylarsine)butane) which have been prepared from prolonged irradiation of  $M(CO)_6$  with the corresponding chelating phosphine or arsine ligands.<sup>23</sup> Tripathi and co-workers have prepared derivatives of the Group VIb hexacarbonyls with 1-(diphenylphosphino)-2-(diphenylarsino)ethane, cis- $[M(CO)_4(dpda)]$  and  $[M(CO)_4(dpda)]_2$  ( $M = Cr, Mo, W$ ), from the thermal reaction of dpda with the corresponding  $M(CO)_6$ .<sup>24</sup> Several mixed amine derivatives were prepared as well, including cis- $[M(CO)_3(dpda)am]$ , cis- $[M(CO)_3(dpda)B]$ , and  $[M(CO)_2(dpda)B]$  ( $am = C_4H_9NH_2$  or  $C_6H_{11}NH_2$ ;  $B = o$ -phenanthroline or 2,2'-bipyridine). The syn-

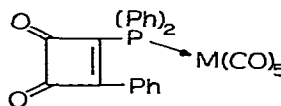
thesis and properties of bis(dimethylphosphino)ethane (dmpe) complexes of Cr, Mo, and W such as fac-fac- $[M_2(CO)_6(dmpe)_3]$  and cis- $[M(CO)_2(dmpe)_2]$  and their iodine oxidation products have also been reported.<sup>25</sup>

The VIb tetracarbonyls of 2,3-bis(diphenylphosphino)maleic anhydride (V) were obtained as air stable, deep blue crystals. Another novel complex obtained during the course of this work was the pentacarbonyl (VI).<sup>26</sup>



M = Cr, Mo, W

(V)



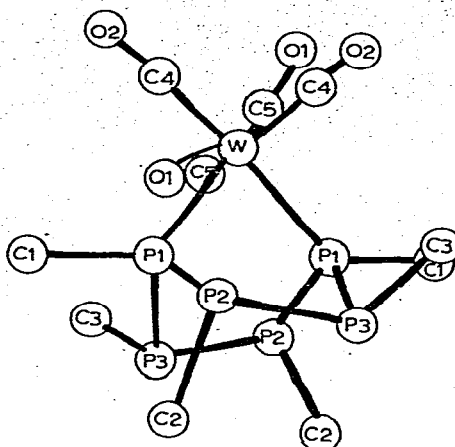
M = Cr, Mo

(VI)

In a study involving reactions of  $CpMn(CO)_2$  (L = CO or CS) with some polydentate organophosphine ligands, Butler and Coville have reported the preparation of the mixed metal species,  $CpMn(CO)(triphos)Cr(CO)_5$  and  $CpMn(CS)(triphos)Cr(CO)_5$  (triphos =  $(Ph_2PCH_2CH_2)_2PPh$ ).<sup>27</sup>

Two papers have appeared which deal with the preparation and X-ray structural analysis of phosphine cage ligands. The cage molecule  $P_4S_3$  was found to bind to a  $Mo(CO)_5$  unit through the unique apical P.<sup>28</sup> The crystal structure of the complex showed only mono-dentate interactions. The reaction of pentamethylcyclopentaphosphine with  $M(CO)_6$  (M = Cr, Mo, W) has led to the isolation of complexes of the general formulae  $(PCH_3)_5 - M(CO)_4$ ,  $(PCH_3)_6M(CO)_4$ ,  $[(PCH_3)_5]_2M_2(CO)_8$  and  $(PCH_3)_9M_2(CO)_6$ .<sup>29</sup> An X-ray structural determination of  $(PCH_3)_6W(CO)_4$  was carried

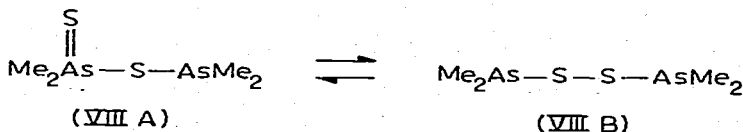
out (VII). The compound previously formulated as  $(PCH_3)_5W(CO)_3$  has been shown to be the dinuclear species  $(PCH_3)_9W_2(CO)_6$ .



(VII)

Reaction of  $M(CO)_4X_2$  ( $M = W, Mo$ ;  $X = Cl, Br, I$ ) with bis-(diphenylstibino)methane (Dpsm) at room temperature yielded the 7-coordinate, non-chelated  $M(CO)_3(Dpsm)_2X_2$  generally in yields of 10-25%.<sup>30</sup> On reflux in  $CH_2Cl_2$ , these tricarbonyls were converted into a proposed 6-coordinate, chelated  $M(CO)_2 - (Dpsm)X_2$  structure. When reacted with  $(CO)_5M'(THF)$  ( $M' = Cr, W$ ),  $(CO)_5M(Ph_2SbCH_2SbPh_2)$  ( $M = Cr, Mo, W$ ) forms symmetric and unsymmetric complexes of the type  $(CO)_5M(Ph_2SbCH_2SbPh_2)M'(CO)_5$ .<sup>31</sup>

Dimethyl(dimethylarsinothio)arsine sulfides (VIII A + VIII B) form desulfurized derivatives of the VIb carbonyls such as  $M(CO)_5(Me_2As-S-AsMe_2)$  and binuclear complexes  $[(CO)_5Cr]_2(\mu-Me_2AsAsMe_2)$ ,  $(CO)_5Cr(\mu-Me_2As-S-AsMe_2)W(CO)_5$ , and  $[(CO)_5W]_2(\mu-Me_2As-S-AsMe_2)$ .<sup>32</sup>





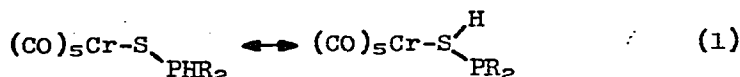
The addition of tetramethyldiarsine to 2,2,4,4-tetramethylbicyclo[1.1.0]butane has been observed to form predominantly cis-1,3-bis(dimethylarsino)-2,2,4,4-tetramethylcyclobutane.<sup>33</sup>

This ligand was shown to behave both as a bridging or chelating ligand with Group VIb carbonyls affording (L-L)M(CO)<sub>4</sub> and (L-L)M<sub>2</sub>(CO)<sub>10</sub> derivatives.

Complexes of (CO)<sub>5</sub>M(tri-t-butylstibine) (M = Cr, Mo and W) have been prepared from M(CO)<sub>6</sub> and [(CH<sub>3</sub>)<sub>3</sub>C]<sub>3</sub>Sb in THF using uv irradiation.<sup>34</sup> The starting material tri-t-butylstibine was prepared from antimonytribromide and t-butylmagnesium chloride. The ir, Raman, and <sup>1</sup>H nmr spectra of these complexes were discussed.

Further work with the thiocarbonyl ligand was presented by Angelici.<sup>35</sup> Lewis acids which were found to complex to the S of W(CO)(dppe)<sub>2</sub>CS included HgCl<sub>2</sub>, HgI<sub>2</sub>, Ag<sup>+</sup>, and W(CO)<sub>5</sub>. The latter complex, formulated as (dppe)<sub>2</sub>(CO)WC≡SW(CO)<sub>5</sub>, was prepared by the labile-ligand technique, utilizing W(CO)<sub>5</sub>(acetone) as precursor.

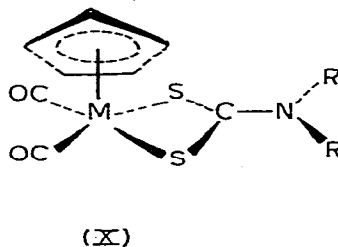
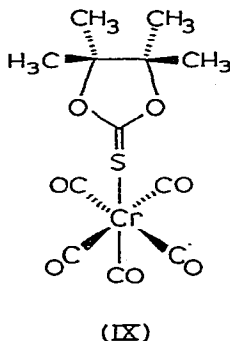
Complexes of the type (OC)<sub>5</sub>MSPHR<sub>2</sub> (M = Cr, Mo; R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>) have been prepared from the reactions of (CO)<sub>5</sub>CrNCCH<sub>3</sub> and (CO)<sub>5</sub>MoTHF with the phosphine sulfides at room temperature.<sup>36</sup> The <sup>1</sup>H nmr and mass spectra indicated that the proton was tautomericly linked either to sulfur or phosphorus, e.g.,



Crystalline yellow, diamagnetic complexes of the form M(CO)<sub>5</sub>tm (M = Cr, Mo, W), where tm = thiomorpholin-3-one

(S-CH<sub>2</sub>CH<sub>2</sub>-NH-CO-CH<sub>2</sub>), were prepared from M(CO)<sub>5</sub>THF and thiomorpholin-3-one.<sup>37</sup> The bonding of the ligand through the sulfur atom was suggested by ir data ( $\nu$ (NH),  $\nu$ (C≡O),  $\nu$ (C=O)) and this was confirmed by the X-ray structural analysis of W(CO)<sub>5</sub>tm. The crystal structure of (thiazolidine-2-thione)pentacarbonyltungsten has also been reported.<sup>38</sup>

The thionocarbonate chromium carbonyl complex (IX) has been prepared from Cr(CO)<sub>6</sub> and 2,3-dimethylbutan-2,3-thionocarbonate in THF in the presence of light.<sup>39</sup>



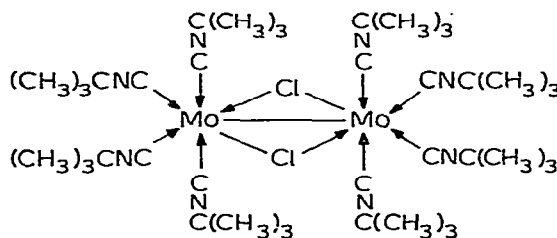
Glass and Shields have reported the preparation and spectral characterization (uv and ir) of the mononuclear tungsten dithiocarbamate complexes CpW(CO)<sub>2</sub>S<sub>2</sub>CN(CH<sub>3</sub>)<sub>2</sub>, CpW(CO)<sub>2</sub>S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, and CpW(CO)<sub>2</sub>S<sub>2</sub>CNC<sub>5</sub>H<sub>10</sub>.<sup>40</sup> The dithiocarbamate ligand is bidentate (X) in these complexes.

Reaction of W(CO)<sub>6</sub> with PhC(=S)CH<sub>2</sub>C(=O)Ph at a 1:2 molar ratio in refluxing pyridine led to the formation of W(PhC(=S)CHC(=O)Ph)<sub>4</sub>.<sup>41</sup>

Several contributions dealing with isocyanide derivatives of Group VIb metal carbonyls have been reported during 1974. The preparation of a series of tert-butyl isocyanide derivatives of Cr, Mo, and W carbonyls ([Me<sub>3</sub>CNC]<sub>n</sub>M(CO)<sub>e-n</sub>, M = Cr,

Mo and W,  $n = 1, 2$  and  $3$ ;  $M = \text{Mo}$  and  $\text{W}$ ,  $n = 4$ ) was reported by King and Saran.<sup>42</sup> An infrared analysis of the effect of degree of substitution on both the  $\nu(\text{CO})$  and  $\nu(\text{CN})$  was included.

Alkyl isocyanide complexes of Mo were prepared by room temperature displacement of acetonitrile ligands in  $(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2(\text{CH}_3\text{CN})_2\text{Cl}$  by  $\text{RNC}$ ,  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $i\text{-Pr}$ ,  $t\text{-Bu}$ ,  $\text{neo-pent}$ , and  $c\text{-hex}$ .<sup>43</sup> At higher temperatures the reaction afforded  $\text{cis}-(\text{RCN})_4\text{Mo}(\text{CO})_2$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ),  $\text{C}_3\text{H}_5\text{Mo}(\text{CO})(\text{RNC})_3\text{Cl}$ ,  $[(\text{RNC})_4\text{MoCl}]_2$  (suggested structure (XI)),  $\text{C}_3\text{H}_5\text{Mo}(\text{RNC})_4\text{Cl}$  ( $\text{R} = t\text{-Bu}$ ), and  $\text{C}_3\text{H}_5\text{Mo}(\text{CO})(\text{RNC})_3\text{CCl}$  ( $\text{R} = \text{neo-pent}$ ).



(XI)

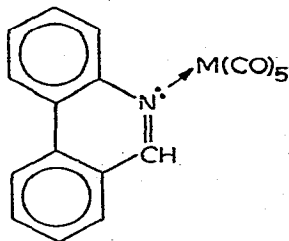
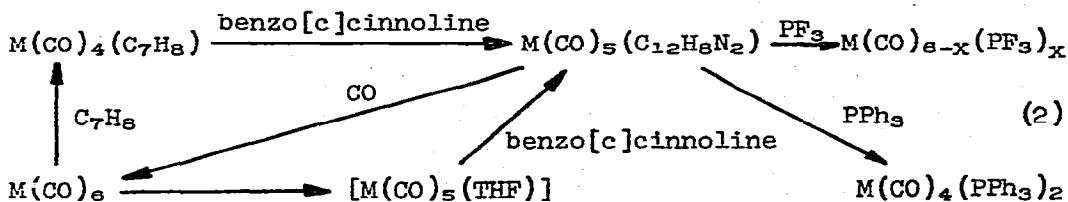
Other reactions of  $\text{tert}$ -butyl isocyanide with cyclopentadienylmolybdenum carbonyl derivatives such as  $\text{CpMo}(\text{CO})_3\text{R}$  and  $\text{CpMo}(\text{CO})_3\text{X}$  yield either insertion products (e.g.,  $\text{CpMo}(\text{CO})_2(\text{t-BuNC})\text{C}(\text{O})\text{R}$ ) or CO displacement products,  $[\text{CpMo}(\text{t-BuNC})_4]^+\text{X}^-$  and  $[\text{CpMo}(\text{CO})_2(\text{t-BuNC})\text{X}]$ .<sup>44</sup> Proton magnetic resonance indicated the last products to exist as mixtures of lateral and diagonal isomers.

Oxy derivatives of  $\text{Mo}(\text{IV})$  compounds, stabilized by isocyanide ligands, were reported by Lippard and Novotny.<sup>45</sup> Thus several preparative methods were used to yield  $[\text{Mo}(\text{O})(\text{X})(\text{CNR})_4]\text{Y}$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ;  $\text{Y} = \text{PF}_6^-$ ,  $\text{I}_3^-$ ,  $\text{IBr}_2^-$ ). Use of  $\text{Et}_2\text{O}$  as solvent in

some reactions led to the production of the 7-coordinate  $[\text{Mo}(\text{CNR})_7]^{++}$ .

Back donation from the metal to the isonitrile ligand ( $d \rightarrow \pi^*$ ) has been demonstrated to be important based on the similarity in the Mo-C(isonitrile) bond distance ( $2.025(10)\text{\AA}$ ) and the Mo-C(carbonyl) bond distances ( $1.973(10)$  and  $1.983(10)\text{\AA}$ ) in  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{I}(\text{CNPh})$ .<sup>46</sup>

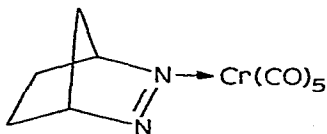
The synthesis of amine substituted metal carbonyl compounds continue to be of interest. For example, Kooti and Nixon have described synthetic routes to mononuclear benzo[c]cinnoline complexes of chromium, molybdenum and tungsten as well as further reactions of these complexes (Scheme 2).<sup>47</sup> Bonding of the benzo[c]cinnoline ligand, as deduced from the  $\nu(\text{CO})$  values, was proposed to occur through the lone pair on nitrogen as opposed to the N=N double bond. The analogous phenanthridine-metal pentacarbonyl complex (XII) was prepared from  $\text{M}(\text{CO})_5\text{THF}$  and phenanthridine.



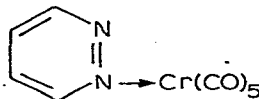
(XII)

2-(MeR<sup>1</sup>C=CR<sup>2</sup>)- and 2-(CH<sub>2</sub>=CR<sup>1</sup>CH<sub>2</sub>CH<sub>2</sub>)-pyridine (R<sup>1</sup>, R<sup>2</sup> = H or Me) have been shown to isomerize via a 1,2-double bond shift upon coordination to Group VIb metal tetracarbonyls<sup>48</sup>. These complexes were prepared from the reaction of the pyridine ligands with M(CO)<sub>4</sub>(norbornadiene) (M = Cr, Mo, W). Similarly 2-(CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)-pyridine undergoes a 1,3-double bond shift in an analogous reaction. The infrared spectra in the ν(CO) region indicate that conformational isomerism involving the plane of coordination of the olefin is not occurring.

The labile ligand method was also used to obtain chromium-carbonyl derivatives of hetero-ring systems possessing a N=N double bond such as (XIII), (XIV), and others.<sup>49</sup> <sup>1</sup>H nmr and ir



(XIII)



(XIV)

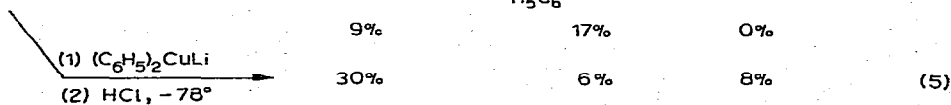
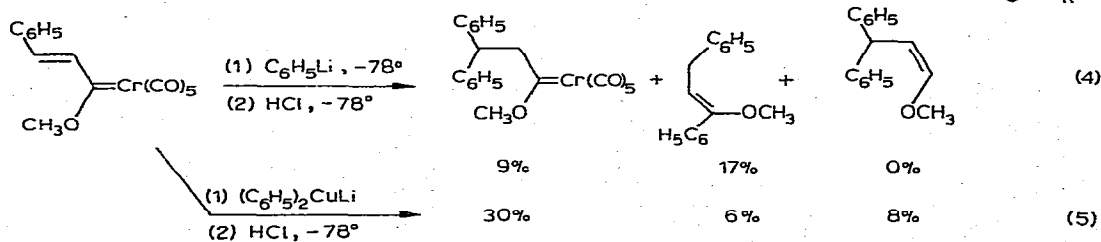
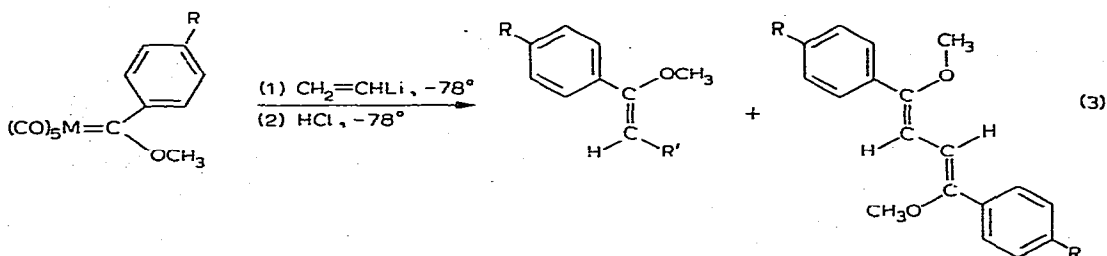
spectra established the bonding of the ligands through a lone pair on N rather than through the double bond. In an accompanying work, the preparations and properties of higher mononuclear derivatives of 2,3-diazabicyclo[2.2.1]hept-2-ene and pyridazine (the ligands of (XIII) and (XIV) above), L<sub>2</sub>Cr(CO)<sub>4</sub> and L<sub>3</sub>Cr(CO)<sub>3</sub>, as well as binuclear complexes (CO)<sub>4</sub>CrL<sub>2</sub>Cr(CO)<sub>4</sub> and (CO)<sub>3</sub>CrL<sub>3</sub>-Cr(CO)<sub>3</sub> containing L as 4-electron bridging ligands, were also described.<sup>50</sup> Fluxional character of the chromium/2,3-diazabicyclo[2.2.1]hept-2-ene ligand bond was observed via <sup>1</sup>H nmr for a (substituted-π-arene)Cr(CO)<sub>2</sub>L system.<sup>51</sup> At room temperature the structure analogous to (XIII) above obtains; at temperatures

of 52 to 95°C, dependent on the  $\pi$ -arene substituent, coalescence of the bridge-head proton signals signifies rapid equilibration of C-N bonds.

Tripathi and co-workers have reported an additional paper dealing with the preparation of amine- and mixed amine-tungsten tricarbonyl derivatives.<sup>52</sup>

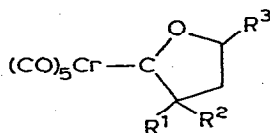
Pyridine may be used as an organic moiety release agent.<sup>53</sup> Thus N-methyl-3-ethyl-, (1,2-dihydropyridine)chromium tricarbonyl reacted with pyridine to release the pure dihydropyridine which could be used for further studies in situ.

Carbene and related complexes. A variety of studies involving reactions of alkoxy-carbene complexes has appeared in the 1974 literature. Casey and Brunsvold have shown that the reaction of vinyl-lithium with  $(CO)_5MC(OCH_3)C_6H_4R$  ( $M = Cr$ ,  $R = H, CH_3$ ;  $M = W$ ,  $R = H$ ) at  $-78^\circ$  followed by treatment with HCl at  $-78^\circ$  gave vinyl ethers and butadienes (eq 3) with no trace of a vinylphenylcarbene complex or its expected decompo-

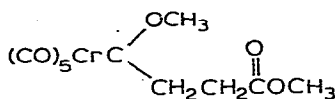


sition products being observed.<sup>54</sup> These products are proposed to be derived from electrophilic attack at the carbon-carbon double bond of a  $\sigma$ -allylmetal intermediate. Additional reactions of  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{CH}=\text{CHC}_6\text{H}_5$  with phenyllithium and lithium diphenylcuprate were also reported (eqs 4 and 5).

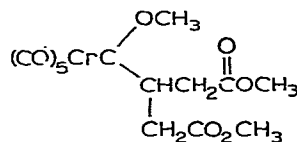
The reaction of  $(\text{CO})_5\text{CrC}(\text{OMe})\text{CH}_2\text{R}$  ( $\text{R} = \text{H}$  or  $\text{CH}_3$ ) with butyllithium to abstract an  $\alpha$ -proton followed by further reaction with epoxides or methyl bromoacetate results in the formation of the alkylated carbene complexes, (XV) and (XVI A) or (XVI B), respectively.<sup>55</sup>



(XV)



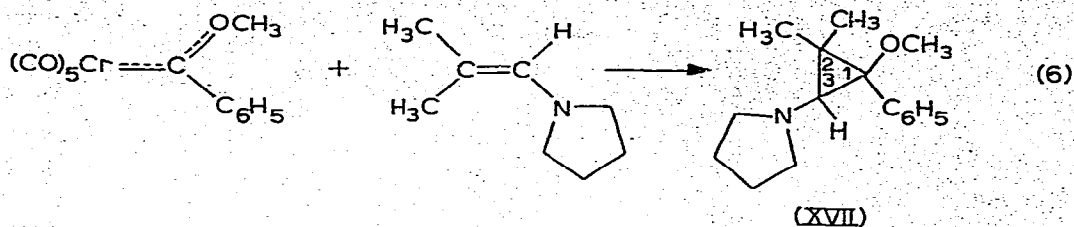
(XVI A)



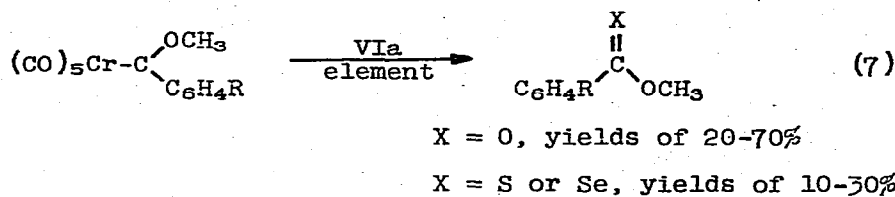
(XVI B)

The acidity of metal carbene complexes was further investigated by Casey and Anderson.<sup>56</sup> Thus  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{CH}_3$  was established to be one of the most acidic neutral carbon acids known by virtue of the fact that *p*-cyanophenol was required to protonate the (triphenylphosphine)iminium ( $\text{PPN}^+$ ) salt of  $(\text{CO})_5\text{CrC}(\text{OMe})\text{CH}_2^-$  in substantial amounts. Interestingly the  $\text{Li}^+$  salt of the anion was more easily protonated whereas the  $\text{HMPA-Li}^+$  solvate behaved similarly to the  $\text{PPN}^+$  salt. The cation dependence was ascribed to  $\text{Li}^+$  stabilization of conjugate bases produced from the protonating agents.

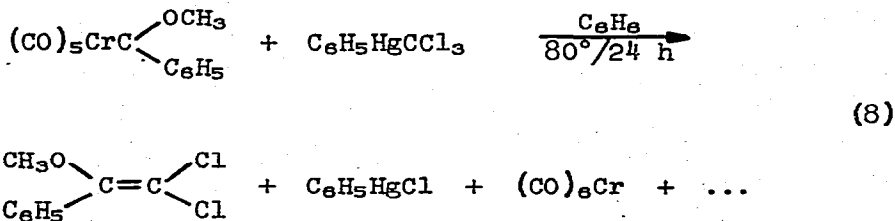
Fischer and co-workers have synthesized the substituted cyclopropane derivative (XVII) employing the chromium carbene complex  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{C}_6\text{H}_5$  (eq 6).<sup>57</sup>



The reactions of chromiumpentacarbonyl(methoxyarylcabene) with VIA elements  $\text{O}_2$ ,  $\text{S}_8$ , and  $\text{Se}_x$  in refluxing hexane, ether or dioxane, respectively, led to the ester derivatives shown in eq 7.<sup>58</sup> de Renzi and Fischer have also shown that



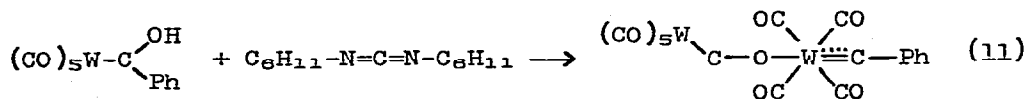
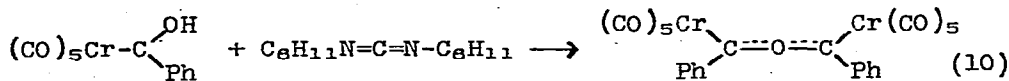
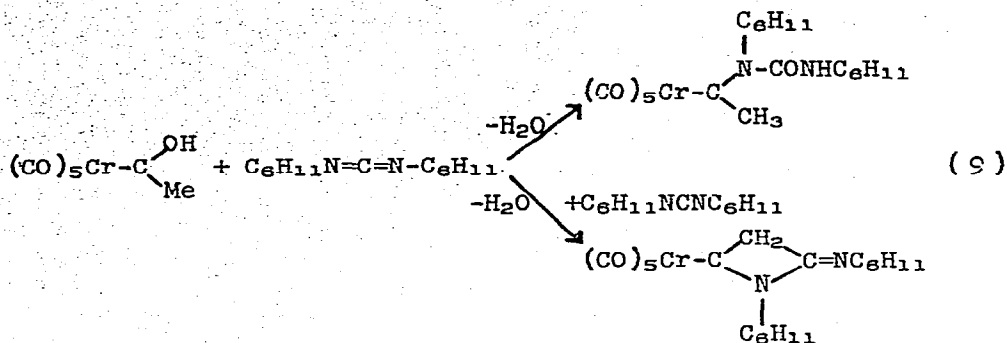
$(\text{CO})_5\text{Cr}(\text{OMe})\text{Ph}$  reacts with phenyl(trihalomethyl)mercury to give the 1,1-dihalo-2-phenylvinyl methyl ethers (eq 8) along with methyl benzoate and benzophenone.<sup>59</sup>



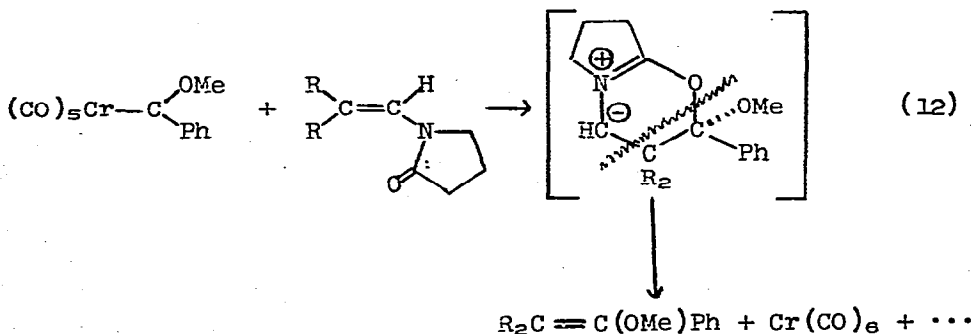
The reactions of chromium- and tungstenpentacarbonyl(hydroxy)carbene with dicyclohexylcarbodiimide (eqs 9, 10, and 11) were also studied by Fischer and co-workers.<sup>60,61</sup>

Other reactions of alkoxy-carbene complexes include the following (eq 12), which used 1-vinyl-2-pyrrolidone as methylene





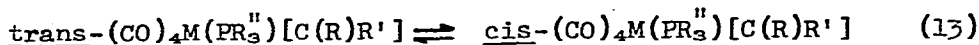
transfer reagent, yielding  $\alpha$ -methoxystyrenes.<sup>62</sup> The cyclic transition state shown was proposed. Under CO pressure, the transition state shown was proposed. Under CO pressure, the



carbene added to vinylpyrrolidones to form enaminoketones or cyclobutanone derivatives.<sup>63</sup> The initial reaction was assumed to be between the carbene ligand and CO, yielding  $\text{Me}(\text{MeO})\text{C}=\text{C}=\text{O}$ , followed by a (2 + 2)-addition to the vinylpyrrolidones.

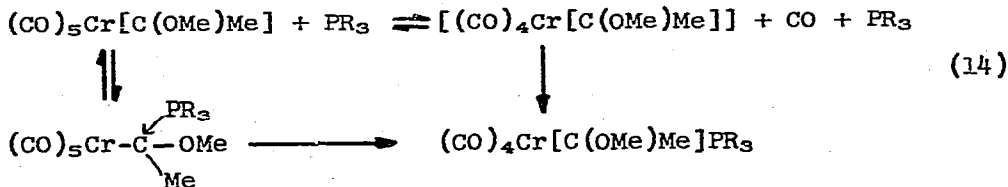
Cleavage of the carbene-chromium bond of  $\text{Cr}(\text{CO})_5\text{C}(\text{OMe})\text{CHR}_2$  by tertiary amines, pyridine, or N-methylpyrrolidine, gave enol ethers,  $\text{MeOCH}=\text{CR}_2$  (40-80% yields).<sup>64</sup> Thermal decomposition of the same carbene complex in decalin gave the dimer of the carbene ligand.

An extensive series of alkoxy- or aminocarbene complexes of the type  $\text{M}(\text{CO})_4(\text{C}(\text{R})\text{R}')\text{PR}_3''$  were prepared by reacting  $\text{PR}_3''$  with the appropriate pentacarbonylcarbene complex at high (70°C) temperatures, or photochemically at lower temperatures.<sup>65,66</sup> The yield of cis isomer was in general higher than that of the trans isomer. In an accompanying paper the thermal isomerization of these compounds was explored.<sup>67</sup> Equilibrium constants at



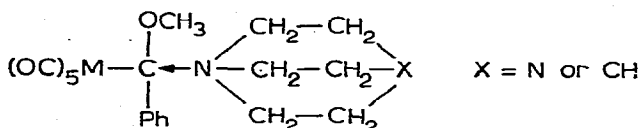
ca. 60°C are in the range of .35 to 11.5 for eq 13 as written, with specific values dependent on M, R, R', R'' and solvent.

Fischer, Fischer, Werner, and Kreiter have further detailed the reversible addition of tertiary phosphines to the carbene carbon of pentacarbonyl(methoxymethylcarbene) metal complexes.<sup>68</sup> From both kinetic and thermodynamic studies, the authors suggested the following scheme for the higher temperature CO displacement reaction (eq 14).



Reactions of amines with carbene complexes have been extended to include the reaction of tertiary, bicyclic amines

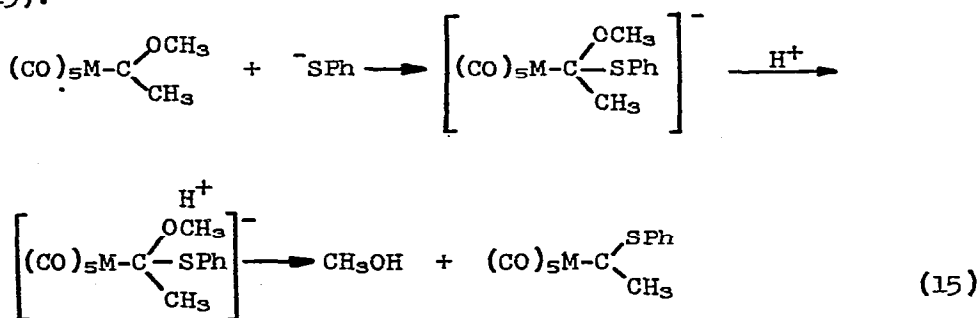
and tungsten- or chromiumpentacarbonyl(methoxyphenylcarbene) yielding the nitrogen analog (XVIII) of the phosphine-carbene adducts.<sup>69</sup> Primary or secondary amines react at the alkoxy group yielding amino carbenes.



(XVIII)

Photolysis of the cis-dicarbene complexes cis-M(CO)<sub>4</sub>L<sub>2</sub> (M = Cr, Mo, W; L = 1,3-dimethyl-4-imidazolin-2-ylidene) has resulted in isomerization to the trans-isomers.<sup>70</sup> These were reconverted to the thermodynamically more stable cis-isomers by heating at 70-173°. Photolysis carried out in pyridine led to both *fac*-Mo(CO)<sub>3</sub>pyL<sub>2</sub> and trans-Mo(CO)<sub>4</sub>L<sub>2</sub>.

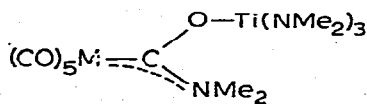
The phenylthiocarbene complexes, [(CO)<sub>5</sub>MC(CH<sub>3</sub>)(SPh)] (M = Cr, Mo, or W), have been prepared by the reaction of [(CO)<sub>5</sub>MC(CH<sub>3</sub>)(OCH<sub>3</sub>)] with NaSPh in benzene/methanol in the presence of HCl.<sup>71</sup> The proposed reaction scheme is as follows (eq 15).



A series of para-substituted phenylthiocarbene derivatives of tungsten pentacarbonyl was also prepared. The complexes were

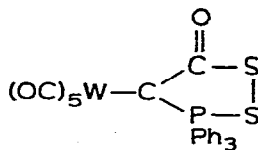
characterized by their infrared, electronic, mass,  $^1\text{H}$  nmr and  $^{13}\text{C}$  nmr spectra.

Petz has reported the synthesis of metal carbene derivatives by addition of  $\text{Ti}(\text{NMe}_2)_4$  to several metal carbonyls, including  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Mo}$  and  $\text{W}$ ).<sup>72</sup> These complexes are proposed to have the structure (XIX). The carbenoid structure of the ligand was deduced from nmr and ir spectral measurements.



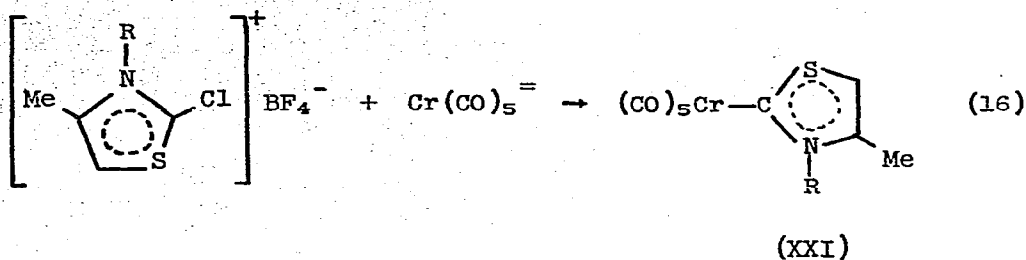
(XIX)

The carbene complexes  $\text{Cr}$ - and  $\text{W}(\text{CO})_5\text{C}(\text{CE})\text{PPh}_3$  ( $\text{E} = \text{O}$  or  $\text{S}$ ) were prepared by reacting  $\text{Ph}_3\text{P}=\text{C}=\text{C}=\text{E}$  with  $(\text{CO})_5\text{M}(\text{CH}_3\text{CN})$  in warm  $\text{Et}_2\text{O}$ ; the corresponding  $\text{Mo}$  complex, by refluxing  $\text{Mo}(\text{CO})_6$  and the ylide in benzene.<sup>73</sup> Formulation of the ligand as a carbene was based on ir, Raman, and mass spectral data. The authors also report an  $\text{S}_2$  addition product (XX) resulting from the reaction of  $\text{W}(\text{CO})_5\text{C}(\text{CO})\text{PPh}_3$  and  $\text{S}_8$ .

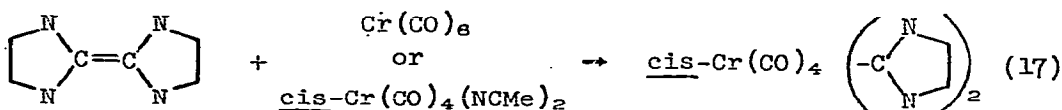


(XX)

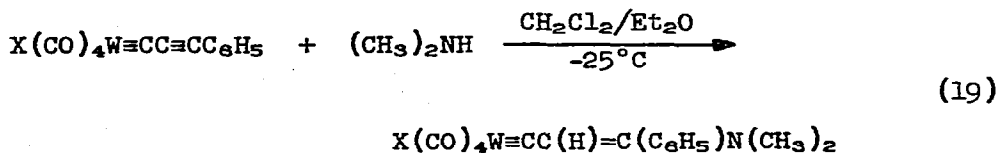
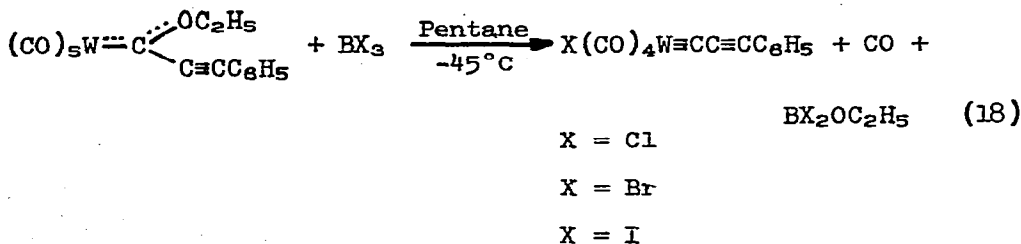
Metal carbonyl anions such as  $\text{Cr}(\text{CO})_5^-$  react with *N*-alkyl-2-chloro-4-methylthiazolium fluoroborate to yield the neutral carbene complex, (XXI) (eq 16).<sup>74</sup>



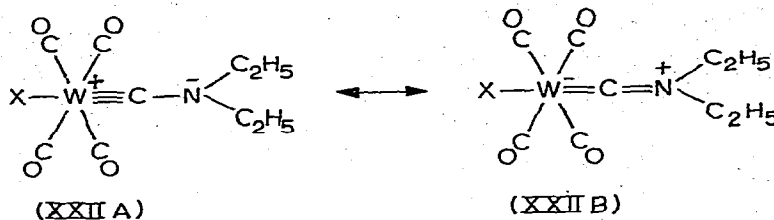
Further application of electron-rich olefins toward the synthesis of transition metal carbene complexes was explored.<sup>75</sup> Among the twenty-four new, stable carbene complexes, the product of eq 17 was reported.



More work on the preparation and reaction of Group VIb metal carbene complexes has been carried out by the Fischer group. trans-Halogeno-phenylacetylenylcarbene-tetracarbonyl-tungsten complexes were prepared according to eq 18 and their reactions with dimethylamine have been investigated (eq 19).<sup>76</sup> Infrared, <sup>1</sup>H, and <sup>13</sup>C nmr spectral properties of all these newly prepared complexes were determined and discussed. In



addition, the carbyne complexes  $XW(CO)_4[CN(C_2H_5)_2]$  (XXII A and XXII B) have been prepared from the alkoxy-aminocarbene derivative  $(CO)_5WC(OC_2H_5)N(C_2H_5)_2$  and  $BX_3$  ( $X = Br$  and  $I$ ).<sup>77</sup> The complexes were characterized by infrared, proton and  $^{13}C$  nmr, and dipole moment measurements.



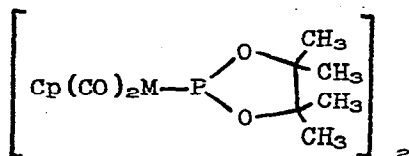
Fischer and Fischer have also reported a new route for the preparation of carbyne complexes starting with  $(CO)_5W[C(OLi)C_6H_5]$  and  $Br_2P(C_6H_5)_3$ .<sup>78</sup> A 31% yield of trans- $Br(CO)_4W=CC_6H_5$  was prepared employing this procedure. A similar yield (29%) of this complex was obtained from reaction of the lithium salt with  $Br(CN)P(C_6H_5)_3$ .

Reaction of 2 equivalents of the Wittig reagent  $Ph_3P=CH_2$  with  $W-$  or  $Cr(CO)_6$  yielded the nucleophilic addition products  $[(CO)_5MC(O)CH=PPh_3]^-Ph_3PCH_3^+$ .<sup>79</sup> In contrast, the ylide of type  $Ph_3P=C=PPh_3$  adds nucleophilically only to  $Mn$  or  $Re$  carbonyl halides; however this compound may coordinate by displacement of weakly held ligands, i.e.,  $(CO)_5WC(PPh_3)_2$  was obtained from  $W(CO)_5THF$ . Interesting ion-pair effects on P-H coupling constants are noted in this rather extensive work.

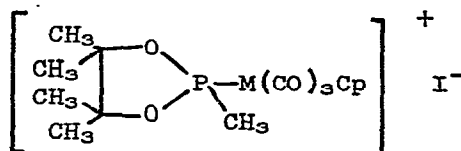
The thiocarboxamido complex,  $CpMo(CO)_2CSNMe_2$ , has been prepared by the reaction of  $Na[CpMo(CO)_3]$  with  $Me_2NCSCl$ .<sup>80</sup> The thiocarboxamido group is believed to be acting as a three-electron donor with bonding to the metal occurring through both

the carbon and sulfur atoms. The sulfur atom can be methylated with  $[\text{Me}_3\text{O}]\text{BF}_4$  to give the derivative  $[\text{CpMo}(\text{CO})_2\text{C}(\text{SMe})\text{NMe}_2]^+$ . In addition, replacement of one CO ligand by  $\text{PPh}_3$  was carried out.

$\pi$ -Cyclopentadienyl,  $\pi$ -arene, and other  $\pi$ -systems. Several studies involving reactions of cyclopentadienyl metal carbonyl anions were reported. The alkylation of  $\text{NaMo}(\text{CO})_3\text{Cp}$  with 2-bromo-2-nitrosopropane yielded a novel, purple volatile  $\text{Me}_2\text{C}(\text{NO})\text{Mo}(\text{CO})_2\text{Cp}$  complex in which the nitrosopropyl group is required to be a 3-electron donor.<sup>81</sup> The analogous alkylation of  $\text{Na}_2\text{M}_2(\text{CO})_{10}$  ( $\text{M} = \text{Cr}, \text{W}$ ) led to the deoxygenated dimethylketimine derivatives,  $\text{Me}_2\text{C}=\text{N}(\text{H})\text{M}(\text{CO})_5$ . Transition metal substituted dioxaphospholanes have been prepared by the reaction of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane with  $\text{Na}[\text{M}(\text{CO})_3\text{Cp}]$  ( $\text{M} = \text{Cr}, \text{Mo}$  and  $\text{W}$ ).<sup>82</sup> These species can be converted into bridged dinuclear complexes upon elimination of CO (XXIII) or to cationic mononuclear complexes when reacted with  $\text{MeI}$  (XXIV).  $\text{Na}[\text{CpW}(\text{CO})_3]$  was found to react with ferrocenoyl chloride to give  $\text{FcCOW}(\text{CO})_3\text{Cp}$  ( $\text{Fc} = \text{ferrocenyl}$ ).<sup>83</sup> This derivative was shown to decarbonylate at  $130^\circ$  to give  $\text{FcW}(\text{CO})_3\text{Cp}$ .



(XXIII)

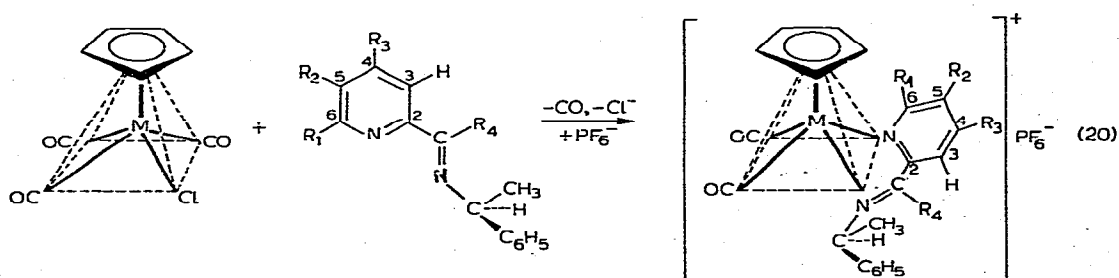


(XXIV)

In a study of the stability of  $\text{Tl}(\text{I})$  salts of metal carbonyl anions toward disproportionation to  $\text{Tl}(\text{0})$  and  $\text{Tl}(\text{III})$ , the compounds  $\text{Tl}[\text{CpM}(\text{CO})_3]$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) and  $\text{Tl}[\text{CpM}(\text{CO})_3]_3$  were pre-

pared and characterized.<sup>84</sup> As in  $Tl[Co(CO)_4]$ , a Tl-metal bond is proposed to explain the  $\nu(CO)$  shift to higher frequencies in  $Tl^{\delta+} \delta^- M(CO)_3 Cp$  as compared to the "free" anion. The order of  $Tl(I)$ -metal carbonyl anion stability was established to be  $Co(CO)_4 \gg CpM(CO)_3 (W > Mo > Cr) > Co(CO)_3 PPh_3 \approx Mn(CO)_5 \gg CpFe(CO)_2$ , that is, decreasing stability with increasing base strength of the anion. Robinson and others later pointed out that a  $pK_a$  of 5 or less for the corresponding transition metal hydrido compound appears to correspond to stable  $Tl(I)$  derivatives.<sup>85</sup>

Brunner and Herrmann have described the synthesis, ir,  $^1H$  nmr and uv spectra of optically active square pyramidal cyclopentadienyldicarbonyl-molybdenum and -tungsten complexes with Schiff bases (eq 20).<sup>86</sup> A detailed study of substituent effects on the intramolecular epimerization (which proceeds via a pseudorotation mechanism) of these complexes was carried out.



In a similar report reaction of  $CpM(CO)_3Cl$  ( $M = Mo$  and  $W$ ) with 8-hydroxyquinoline (HL) and 7-carboxy-8-hydroxyquinoline (HL') led to the formation of the  $CpM(CO)_2L$  and  $CpM(CO)_2L'$  derivatives as enantiomer pairs with cis-coordination via the N and phenolic O atoms.<sup>87</sup>

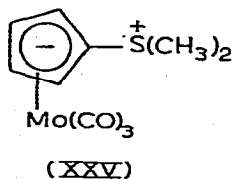
Ether solutions of  $CpM(CO)_3Cl$  ( $M = Mo, W$ ) react with  $Ph_2C=N-Li$  to yield  $CpM(CO)_2Ph_2CNCPh_2$ ; however the addition of



substrates such as  $\text{Ph}_2\text{C}=\text{O}$ ,  $\text{PhCN}$ , trans- $\text{PhCH}=\text{CHPh}$  and others to the reaction mixture changes the course of the reaction yielding the blue solid  $[\text{CpM}(\text{CO})_2\text{N}:\text{CPh}_2]_2$ .<sup>88</sup>

Barnett and co-workers have synthesized the complexes trans- $\text{CpM}(\text{CO})_2\text{L}(\text{COCH}_3)$  [ $\text{M} = \text{Cr}$ ,  $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{P}(\text{p-CH}_3\text{OC}_6\text{H}_4)_3$ ,  $\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2$ ;  $\text{M} = \text{W}$ ,  $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{P}(\text{p-CH}_3\text{OC}_6\text{H}_4)_3$ ,  $\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2$ ,  $\text{P}(\text{n-C}_4\text{H}_9)_3$ ] by the direct reaction of  $\text{CpM}(\text{CO})_3(\text{COCH}_3)$  and the phosphine in acetonitrile solution.<sup>89</sup> Spectral properties (ir, nmr, and mass spectra) of these derivatives are discussed. In addition, the relative metal-carbon bond strengths in the Group VIb triad ( $\text{W} \gg \text{Mo} \geq \text{Cr}$ ) were deduced from the ease of substitution of CO with phosphines as well as the ease of decarbonylation of the acetyl products. A higher valent Mo cyclopentadienyl complex,  $\text{CpMoCl}_2(\text{OR})_2$  ( $\text{R} = \text{alkyl group}$ ), was prepared by the reaction of  $\text{MoCl}_3(\text{OR})_2$  with cyclopentadiene or  $\text{NaC}_5\text{H}_5$  in THF.<sup>90</sup>

The preparation of dimethylsulfoniumcyclopentadienylidemolybdenum tricarbonyl (XXV) has been reported from reaction of dimethylsulfoniumcyclopentadienylide with  $(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3$  in diglyme at room temperature.<sup>91</sup> The complex is a yellow, air-stable species which decomposes at  $173\text{--}175^\circ$ . The structure corresponding to (XXV) was established by ir,  $^1\text{H}$  nmr and mass spectra.  $(\text{h}^5\text{-C}_5\text{H}_4\text{R})\text{Mo}(\text{CO})_2(\text{CN})_3$  and  $\text{K}_2[(\text{h}^5\text{-C}_5\text{H}_4\text{RMO}(\text{CN})_5)]$



( $\text{R} = \text{H}$  or  $\text{Me}$ ) have been prepared from the reaction of  $\text{C}_5\text{H}_4\text{RMO}(\text{CO})_2\text{I}_3$  and  $\text{KCN}$ .<sup>92</sup>

The 16-electron species,  $\text{CpMCl}(\text{RC}\equiv\text{CR})_2$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $\text{R} = \text{CF}_3$ ,  $\text{Me}$  or  $\text{CO}_2\text{Me}$ ) were characterized by X-ray crystallography and were shown to react with  $\text{Ph}_3\text{P}$  to yield  $\text{CpMCl}(\text{PPh}_3)(\text{RC}\equiv\text{CR})_2$ .<sup>93</sup> With  $\text{TlC}_5\text{H}_5$  a rather complex 18-electron structure is obtained which involves addition of  $\text{C}_5\text{H}_5$  to one of the acetylene groups and bonding of the cyclopentadienyl ring to the metal via a  $h^3$  mode.

The production of other 16-electron species was proposed in investigations of bis-cyclopentadienyl compounds of VIb metals. The reaction of  $\text{Cp}_2\text{MoH}_2$  with several azo or diazo compounds was described by Otsuka and co-workers.<sup>94</sup> Among the products were the air-stable and substitution inert  $\text{Cp}_2\text{Mo}(\text{trans-PhN=NPh})$ , with none of the expected orthometallated product observed. Other azo compounds led to formation of metallocycles such as  $\text{Cp}_2\text{MoN}(\text{COR})\text{N}=\text{C}(\text{R})\text{O}$  and  $\text{Cp}_2\text{Mo}[\sigma\text{-NN}=\text{C}(\text{OH})\text{N}(\text{Ph})\text{CO}]_2$ . Some of the products are explained by the *in situ* preparation of the coordinatively unsaturated  $\text{Cp}_2\text{Mo}$  reactive species. Brintzinger's group further investigated the reactivity of this 16-electron species which was produced photochemically in toluene.<sup>95</sup> Similar to Otsuka's azobenzene complex, the acetylene addition product,  $\text{Cp}_2\text{Mo}(\text{HC}\equiv\text{CH})$  is a stable, sublimable solid. The corresponding photolysis of  $\text{Cp}_2\text{W}(\text{CO})$  in toluene and in the presence of alkynes gave comparable amounts of  $\text{Cp}_2\text{W}(\text{RC}\equiv\text{CR})$  and the hydrogen insertion product of the solvent,  $\text{Cp}_2\text{W}(\text{H})\text{C}_6\text{H}_4\text{CH}_3$ .

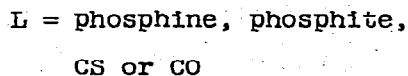
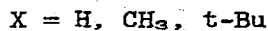
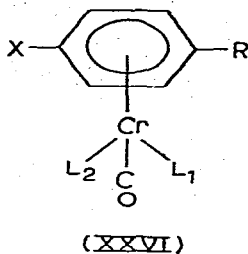
The reaction of  $\text{Cp}_2\text{MoH}_2$  with white phosphorus in hot toluene produces a  $\text{P}_2$  adduct, unstable in air, and formulated as a H-P-P-H derivative, similar to the ethylene complex  $\text{Cp}_2\text{Mo}(\text{H}_2\text{C}=\text{CH}_2)$ .<sup>96</sup> On the other hand irradiation of  $\text{Cp}_2\text{WH}_2$ , in the presence of mesitylene, yielded the rather air stable bis-alkyl derivative,  $\text{Cp}_2\text{W}(\text{CH}_2\text{-3,5-Me}_2\text{C}_6\text{H}_3)_2$ .<sup>97</sup>

Alkyl-olefin cationic complexes,  $[\text{Cp}_2\text{M}(\text{C}_2\text{H}_4)\text{R}]^+$ , of molybdenum and tungsten have been prepared from the reaction of the neutral ethylene derivatives  $\text{Cp}_2\text{M}(\text{C}_2\text{H}_4)$  with the alkyl halides  $\text{MeI}$  or  $\text{PhCH}_2\text{Br}$ .<sup>98</sup> In addition,  $[\text{Cp}_2\text{M}(\text{PPh}_3)\text{Me}]\text{PF}_6$  ( $\text{M} = \text{Mo}$  and  $\text{W}$ ) derivatives were synthesized via the reaction of  $[\text{Cp}_2\text{M}(\text{PPh}_3)\text{Br}]\text{PF}_6$  with methylmagnesium chloride. Still other syntheses of new bicyclopentadienyl VIB metal complexes included those of  $\text{Cp}_2\text{M}(\text{O})\text{L}_2$  ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ;  $\text{L} = \text{CN}$ ,  $\text{NCO}$ ,  $\text{SCN}$ ,  $\text{N}_3$ ,  $\text{SMe}$ ,  $\text{SEt}$ ,  $\text{SPr}$ , and  $\text{SBu}$ ).<sup>99</sup> The azide derivatives were shown to be highly explosive.

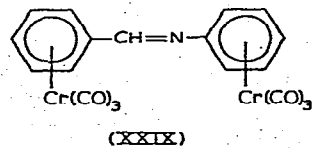
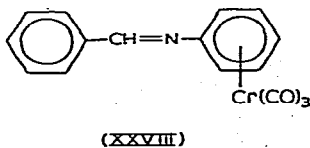
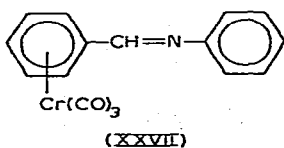
Many new and some improved syntheses of  $\text{h}^6$ -arene compounds were reported. Moser and Rausch have demonstrated the utility of  $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$  (which does not sublime under reaction conditions) as opposed to  $\text{Cr}(\text{CO})_6$  in the preparation of arenechromium tricarbonyl derivatives.<sup>100</sup> In this manner thiophene,  $\text{Me}_3\text{CPh}$ ,  $\text{PhSiMe}_3$  and  $\text{PhI}$ , when reacted with  $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$  in refluxing dioxane, produced the corresponding arene derivatives. In a related process, Rausch also reported an improved synthesis of benzenechromium tricarbonyl requiring the refluxing under nitrogen of equal volumes of benzene and 2-picoline with  $\text{Cr}(\text{CO})_6$ .<sup>101</sup> This procedure was however not applicable to preparing the molybdenum and tungsten analogs. Instead the bis(2-picoline)tetracarbonylmolybdenum and (2-picoline)pentacarbonyltungsten derivatives were produced. In a similar approach, treatment of  $\text{py}_3\text{Mo}(\text{CO})_3$  with a variety of arene ligands in ether containing  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  at  $20^\circ$  has afforded good yields (56-71%) of (arene)- $\text{Mo}(\text{CO})_3$  derivatives where arene =  $\text{PhMe}$ , mesitylene,  $\text{BuPh}$ , tetralin,  $p\text{-(Me}_3\text{C)}_2\text{C}_6\text{H}_4$ ,  $\text{PhOMe}$ ,  $\text{PhCH}:\text{CH}_2$ ,  $\text{PhCH}_2\text{CH}_2\text{CH}:\text{CH}_2$ ,  $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{Br}$ ,  $\text{PhCH}_2\text{CH}_2\text{OMe}$ ,  $\text{PhCH}_2\text{CH}_2\text{COMe}$ , and 2',4',6'- $\text{Me}_3\text{C}_6\text{H}_2\text{COMe}$ .<sup>102</sup>

Several derivatives of arenechromium tricarbonyl (XXVI)

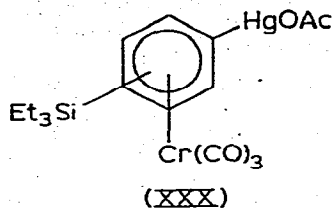
including those with a chiral center at chromium have been synthesized by Jaouen and Dabard.<sup>103</sup> Spectral data (ir and nmr) were obtained and discussed in detail.



Other preparations of arene tricarbonyls include the following. Compounds of  $\text{RC}_6\text{H}_5\text{Cr}(\text{CO})_3$  ( $R = \text{Me}_2\text{N}, \text{MeO}, \text{Me}, \text{H}$ ) were obtained in good yields by treatment of bis(phenylchromiumtricarbonyl)mercury with  $\text{LiAlH}_4$ .<sup>104</sup> Anisole tricarbonyl complexes of molybdenum and tungsten have been prepared and their decomposition reactions studied by Nesmeyanov and co-workers.<sup>105</sup> Treatment of  $\text{PhCH:NPh}$  with  $\text{Cr}(\text{CO})_6$  has led to the formation of three tricarbonylchromium complexes of *N*-benzylideneaniline (XXVII, XXVIII, and XXIX).<sup>106</sup> Phenyltriethylsilane reacted with  $\text{Cr}(\text{CO})_6$

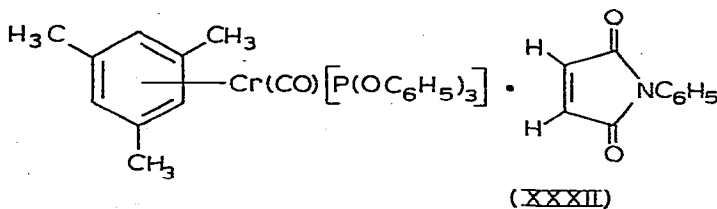
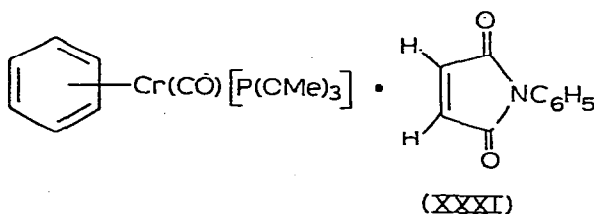


in diglyme/octane ( $145-50^\circ$ ) to give a 65% yield of  $(\eta^6\text{-C}_6\text{H}_5\text{SiEt}_3)\text{-Cr}(\text{CO})_3$  which when reacted with  $\text{Hg}(\text{OAc})_2$  was mercurated thus producing XXX.<sup>107</sup>



Benzocycloheptatrienechromium tricarbonyl was also prepared by thermal displacement of three CO groups in  $\text{Cr}(\text{CO})_6$ .<sup>108</sup> Infrared and nmr data suggest the ligand to bind through the 6-membered ring. Mass spectral analysis of the compound was given.

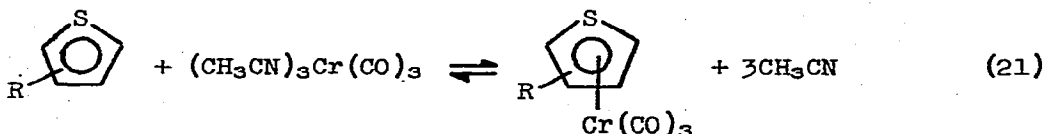
Nasielski and Denisoff have described the preparation of the first neutral asymmetric (arene)chromium tricarbonyl derivatives of the type  $(\text{arene})\text{Cr}(\text{CO})\text{LL}'$ , where L = phosphite and L' = N-substituted maleimide (XXXI and XXXII).<sup>109</sup> The vinylic protons are diastereotopic and display a temperature-dependent nmr spectrum.



Reactions of sodium cyanotrihydroborate or sodium cyanotriphenylborate with  $\text{M}(\text{CO})_3$  (M = Cr, Mo, and W) in boiling

glyme resulted in formation of the yellow, anionic complexes,  $[\text{H}_3\text{BCNM}(\text{CO})_5]^-$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) and  $[(\text{C}_6\text{H}_5)_3\text{BCNM}(\text{CO})_5]^-$  ( $\text{M} = \text{Mo}, \text{W}$ ), respectively, where complexation has occurred through a cyano group.<sup>110</sup> On the other hand reaction of  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}$  and  $\text{W}$ ) with sodium tetraphenylborate in boiling diglyme gave the yellow anions  $[(\text{C}_6\text{H}_5)_2\text{B}[\text{C}_6\text{H}_5\text{M}(\text{CO})_3]_2]^-$  ( $\text{M} = \text{Cr}, \text{W}$ ) where two of the phenyl rings are  $\pi$ -bonded to two  $\text{M}(\text{CO})_3$  moieties.

$\pi$  complexes of  $\text{Cr}(\text{CO})_3$  and substituted thiophenes have been prepared from the reaction of  $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$  with the heterocycles (eq 21).<sup>111</sup> The relative retention times and the decomposition of these complexes have been studied by gas-liquid chromatography. In addition, ligand substitution reactions of these (thiophene) $\text{Cr}(\text{CO})_3$  derivatives with substituted benzenes to afford (arene) $\text{Cr}(\text{CO})_3$  have been investigated.



Less conventional  $\pi$ -complexes include those of borazines such as  $\text{Me}_3\text{B}_3\text{N}_3\text{H}_3\text{Cr}(\text{CO})_3$  which was synthesized by means of a ring exchange reaction involving  $\text{Et}_3\text{B}_3\text{N}_3\text{Me}_3\text{Cr}(\text{CO})_3$  and  $\text{Me}_3\text{B}_3\text{N}_3\text{H}_3$ .<sup>112</sup> The new compound was characterized by means of ir, nmr, uv and mass spectral data. Other borazine-metal complexes,  $\text{Cr}(\text{CO})_3(\text{R}_3\text{B}_3\text{N}_3\text{R}^1_3)$  ( $\text{R} = \text{Pr}$  and  $\text{R}^1 = \text{Me}$ ,  $\text{R} = \text{Me}$  and  $\text{R}^1 = \text{Pr}$ ,  $\text{R} = i\text{-Pr}$  and  $\text{R}^1 = \text{Me}$ ,  $\text{R} = \text{Me}$  and  $\text{R}^1 = i\text{-Pr}$ ), were prepared from  $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$  and the corresponding borazine in dioxane.<sup>113</sup> These derivatives were more labile than the isomeric complex  $\text{Cr}(\text{CO})_3(\text{Et}_3\text{B}_3\text{N}_3\text{Et}_3)$ .

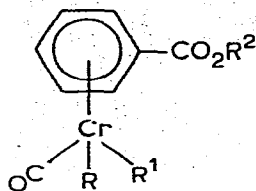
Several syntheses of bis-arene compounds were reported; the most dramatic one made use of the metal atom synthesis technique. The synthetic potential of the co-condensation technique was demonstrated by preparation of a series of bis-arene sandwich complexes of W and Mo, arene = anisole, fluorobenzene, methylbenzoate, N,N-dimethylaniline, etc.<sup>114</sup> Similarly, the preparation of a group of bis(arene)chromium compounds has appeared in a German patent. These include arene = m-diisopropylbenzene, cumene, and biphenyl(m-diisopropylbenzene).<sup>115</sup>

An improved synthesis of the sandwich compounds  $(C_5H_5)_2M(C_7H_7)$  ( $M = Cr$  and  $Mo$ ) from the reaction of  $MCl_3 \cdot 3THF$ ,  $C_7H_8$ ,  $C_5H_6$  and  $i-C_3H_7MgBr$  in THF at  $-20^\circ$  has been reported.<sup>116</sup>

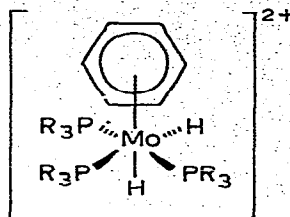
The following compounds were separated and purified by molecular distillation:  $(\eta^6-C_6H_6)Mo(\eta^6-C_6H_5Et)$ ,  $(\eta^6-C_6H_5Et)_2Mo$ ,  $(\eta^6-C_6H_5Et)Mo(\eta^6-C_6H_4Et_2)$ , and  $(\eta^6-C_6H_4Et_2)_2Mo$ .<sup>117</sup>

Some chemical properties of  $\eta^6$ -arene compounds are given in the next three works. Irradiation of derivatives of benzene-chromiumtricarbonyl (XXXIII A) ( $R = R^1 = CO$ ,  $R^2 = Me$ ) with cis-cyclooctene and treatment of the product with  $CS_2/PPh_3$  has afforded (XXXIII B) ( $R = CS$ ,  $R^1 = CO$ ,  $R^2 = Me$ ).<sup>118</sup> Further irradiation of this derivative in the presence of  $P(OEt)_3$  gave (XXXIII C) ( $R = CS$ ,  $R^1 = P(OEt)_3$ ,  $R^2 = Me$ ). Saponification of this derivative gave the asymmetric chromium derivative (XXXIII D) ( $R = CS$ ,  $R^1 = P(OEt)_3$ ,  $R^2 = H$ ) which had a  $pK_a$  value of 5.20, indicating that  $\pi$ -backbonding to CS was greater than to CO in this derivative.

The increased basicity of  $(\eta^6\text{-arene})Mo(PR_3)_3$  complexes over the analogous  $(\eta^6\text{-arene})Cr(CO)_3$  allowed for both mono- and diprotonation of the Mo complex.<sup>119</sup> The structure of the latter product was proposed to be (XXXIV).



(XXXIII A-D)



(XXXIV)

Arenetricarbonylchromium complexes have been shown to form charge-transfer molecular complexes via the  $\pi$ -coordinated benzene ring and electron acceptors such as 1,3,5-trinitrobenzene and TCNE.<sup>120</sup>

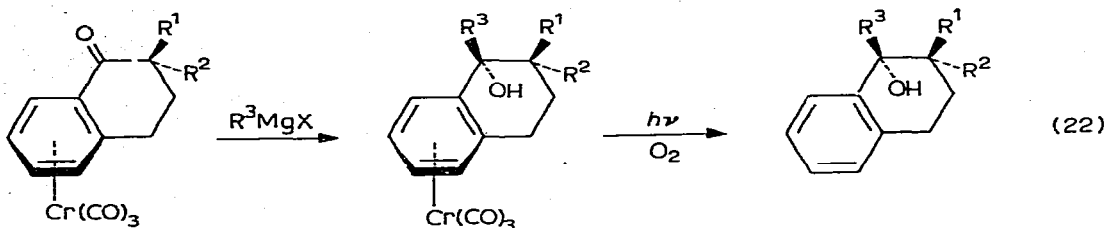
Many reports of mechanistic and synthetic importance dealt with reactions at the  $\pi$ -cyclopentadienyl,  $\pi$ -arene,  $\pi$ -tropylium or  $\pi$ -allylic site of such metal-bound groups. These are grouped together as follows.

The complexes  $[(\eta^6\text{-arene})\text{Cr}(\text{CO})_2\text{NO}]^+$  (arene =  $\text{C}_6\text{H}_n\text{Me}_{6-n}$ ,  $n = 0-2$ ) are decidedly less reactive toward nucleophilic attack on the ring than are the isostructural and isoelectronic  $(\eta^6\text{-arene})\text{Mn}(\text{CO})_3^+$ .<sup>121</sup> Both the Cr and Mn analogs add  $\text{H}^-$ ,  $\text{D}^-$ , and  $\text{Me}^-$  *exo* to the ring yielding neutral cyclopentadienyl derivatives, however the manganese arene complexes are also reactive toward  $\text{CN}^-$ ,  $\text{Ph}^-$ ,  $\text{N}_3^-$ ,  $\text{NCO}^-$  and other less common nucleophiles.

Semmelhack and Hall investigated the intermediates in the synthetically important nucleophilic addition reactions to the ring of ( $\pi$ -chlorobenzene)chromium tricarbonyl.<sup>122</sup> Protonation of the  $(\eta^6\text{-C}_6\text{H}_5\text{Cl})\text{Cr}(\text{CO})_3$ /isobutyronitrile carbanion system, followed immediately by iodine oxidation, yielded not only  $\text{C}_6\text{H}_5\text{Cl}$  and phenylisobutyronitrile, but also *o*- and *m*-chloro(2-cyano-2-propyl)benzene and a series of dihydrobenzene compounds. Comments on possible mechanisms were included.

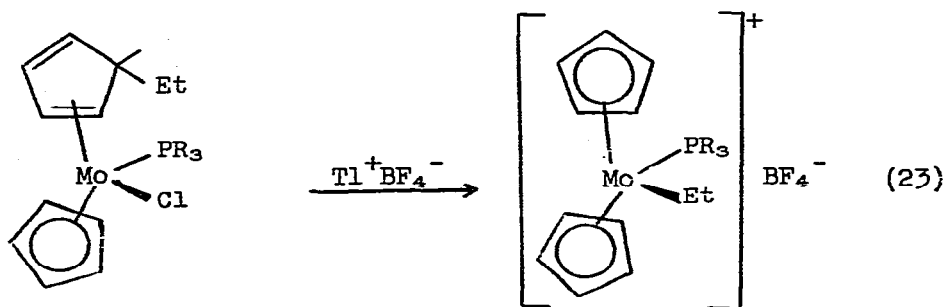


The following reaction sequence (eq 22) illustrates the application of  $\pi$ -arenechromiumtricarbonyl derivatives in the synthesis of optically active tertiary alcohols.<sup>123</sup> Treatment

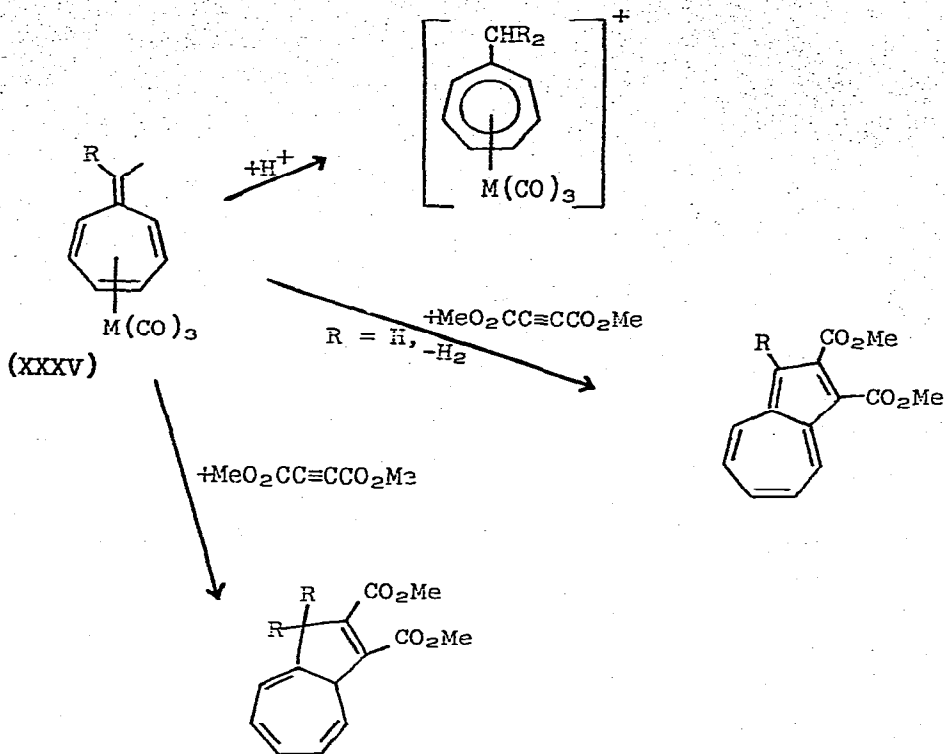


of  $(\eta^6\text{-C}_6\text{H}_5\text{Et})\text{Cr}(\text{CO})_3$  with  $\text{Me}_3\text{CLi}$  followed by  $\text{Ce}(\text{IV})$  oxidation has afforded 32% *m*- and 9% *p*- $\text{Me}_3\text{CC}_6\text{H}_4\text{Et}$ .<sup>124</sup>

A reversible metal-to-ring transfer of an ethyl group was reported by Green and Benfield in studies of alkynyl, alkyl, and olefin complexes of bis( $\pi$ -cyclopentadienyl)molybdenum or tungsten.<sup>125</sup> For example, see eq 23.

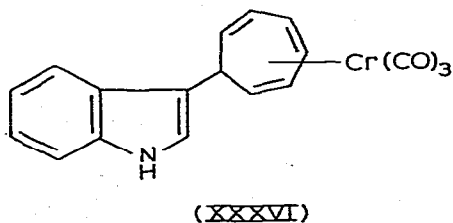


Reaction of  $[\pi\text{-C}_7\text{H}_7\text{Mo}(\text{CO})_3]\text{BF}_4$  with triphenylphosphine at room temperature has afforded good yields of  $[\pi\text{-C}_7\text{H}_7\text{Mo}(\text{CO})_2\text{PPh}_3] - \text{BF}_4$ .<sup>126</sup> Reduction of this species with  $\text{NaBH}_4$  yields the neutral cycloheptatriene complex  $(\text{C}_7\text{H}_8)\text{Mo}(\text{CO})_2\text{PPh}_3$ . Heptafulvene complexes of chromium-, molybdenum-, and tungstentricarbonyl (XXXV)



have been found to react with electrophiles such as  $\text{HPF}_6$  (but not  $\text{Et}_3\text{O}^+\text{BF}_4^-$ ) and dienophiles at the exocyclic double bond, in marked contrast to the analogous iron compounds.<sup>127</sup>

The tropylium complex  $[\pi\text{-C}_7\text{H}_7\text{Cr}(\text{CO})_3][\text{BF}_4^-]$  has been shown to undergo electrophilic addition with indole to provide orange crystals of the substituted triene (XXXVI).<sup>128</sup> The structure



is supported by  $^1\text{H}$  nmr, ir, and mass spectral data. This reac-

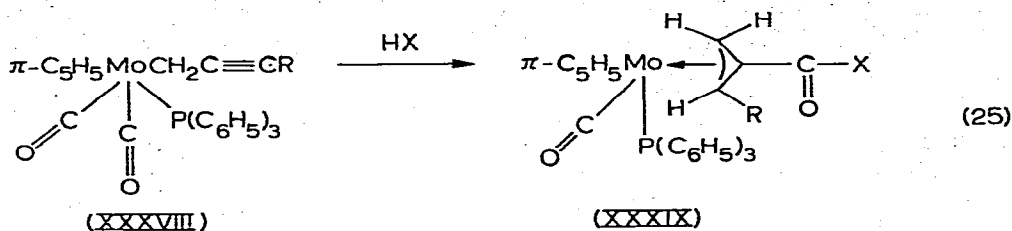
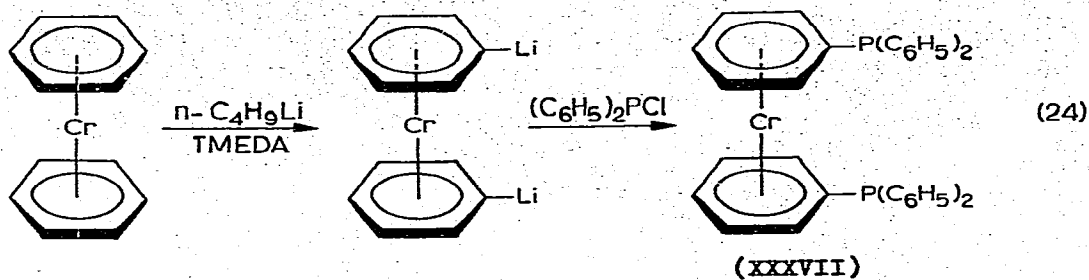
tion represents a more general reaction under investigation by these workers which involves the attack of an aromatic substrate by cationic organometallic complexes.

Reactions of the diazonium salts,  $[p\text{-RC}_6\text{H}_4\text{N}_2]\text{X}$  ( $\text{R} = \text{H}$ ,  $\text{X} = \text{PF}_6$ ;  $\text{R} = \text{OMe}$  and  $\text{NO}_2$ ,  $\text{X} = \text{BF}_4$ ), with  $(\text{C}_6\text{Me}_6)\text{Cr}(\text{CO})_3$  affords stable, crystalline salts of the form  $[(\text{C}_6\text{Me}_6)\text{Cr}(\text{CO})_2(p\text{-RC}_6\text{H}_4\text{N}_2)]\text{X}$ .<sup>129</sup> In THF, hydride ion, from  $\text{NaBH}_4$ , was shown to add preferentially to the arene ligand as opposed to the arylazo ligand to produce neutral cyclohexadienyl derivatives,  $(\text{C}_6\text{Me}_6\text{H})\text{Cr}(\text{CO})_2(p\text{-RC}_6\text{H}_4\text{N}_2)$ . On the other hand  $(\text{C}_6\text{Me}_6)\text{Cr}(\text{CO})_2(\text{PPh}_3)$  reacted with  $p\text{-RC}_6\text{H}_4\text{N}_2^+$  to yield the yellow, paramagnetic cation  $[(\text{C}_6\text{Me}_6)\text{Cr}(\text{CO})_2\text{PPh}_3]^+$ .  $(\text{C}_6\text{Me}_6)\text{Mo}(\text{CO})_3$  also reacted with  $p\text{-RC}_6\text{H}_4\text{N}_2^+$  to yield complexes analogous to those of chromium.

Reactions of  $[(\text{h}^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{CO})(\text{h}^3\text{-C}_3\text{H}_5)]\text{PF}_6$  with  $\text{I}^-$  gave the CO displacement product,  $(\text{h}^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{h}^3\text{-C}_3\text{H}_5)\text{I}$ ; with  $\text{BH}_4^-$  and  $\text{S}_2\text{CNMe}_2^-$  however reaction was at the  $\pi$ -allylic site giving  $(\text{h}^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{CO})(\text{h}^2\text{-H}_2\text{C}=\text{CHMe})$  and  $(\text{h}^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{-}(\text{h}^2\text{-CH}_2=\text{CHCH}_2\text{SC}(=\text{S})\text{NMe}_2)$ .<sup>130</sup>

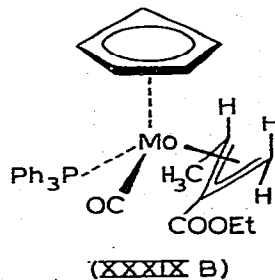
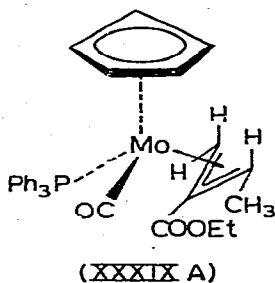
Bis(diphenylphosphino- $\text{h}^6$ -benzene)chromium(0) (XXXVII) has been prepared by the pathway shown below (eq 24).<sup>131</sup> Both phosphines were found to undergo methylation reactions with methyl iodide to yield the dicationic species.

Some very interesting new  $\pi$ -allyl syntheses have been reported. Stable  $\sigma$ -propargylic compounds of molybdenum have been prepared (XXXVIII).<sup>132</sup> Reactions of these species with nucleophilic reagents (HX) have led to the preparation of  $\pi$ -allyl derivatives (XXXIX, eq 25) which were shown to exist in two structural forms (XXXIX A and XXXIX B) in a 2:3 ratio, respectively.



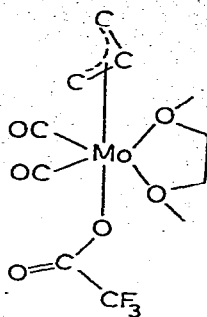
R = H; X = OCH<sub>3</sub>, SPh, OC(CH<sub>3</sub>)<sub>3</sub>

R = CH<sub>3</sub>; X = OCH<sub>2</sub>CH<sub>3</sub>



The new  $\pi$ -allyl complexes  $(\pi\text{-R}'\text{C}_3\text{H}_4)\text{M}(\text{CO})_2\text{L}_2\text{X}$  (M = Mo or W; R' = H or Me; X = Cl, Br, I or NCS; L<sub>2</sub> = 1,2-ethanediyldenedi-imines or 2-pyridinaldimines) (XL, XLI and XLII) have been prepared via reaction of the bis(acetonitrile) derivatives with L<sub>2</sub>.<sup>133</sup> The solvent dependence of the infrared ( $\nu_{\text{CO}}$ ) and electronic spectra (metal to ligand charge transfer) of these derivatives was investigated.

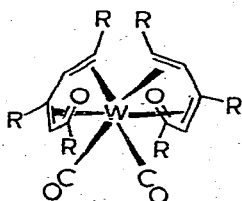




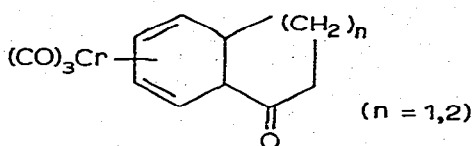
(XLIV)

Several other reports have dealt with the syntheses or reactions of  $\pi$ -systems. For example, another demonstration of the efficacy of the co-condensation technique in previously declared difficult to impossible synthesis was presented by Skell and co-workers.<sup>137</sup> Reaction of atomic W or Mo with 1,3-butadiene yielded sublimable, stable tris(butadiene)tungsten (white crystals) or -molybdenum (yellow crystals).

2,2,4,6-Tetramethyl-2H-pyrene afforded some of the isomeric 4,6-dimethyl-3,5-heptadien-2-one when reacted with  $(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3$ , and dicarbonylbis(4-6-dimethyl-3,5-heptadien-2-one)tungsten was produced in low yield.<sup>138</sup> Spectral measurements indicated the structure (XLV). In addition, 6-methyl-2H-thiopyrene was found to react with  $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$  to give tricarbonyl(6-methyl-2H-thiopyrene)chromium, a new heterocyclic  $\pi$ -complex where thiopyrene acts as a six-electron donor ligand. Chromium tricarbonyl complexes of the type (XLVI) have been prepared where the ketonic oxygen serves as the sixth ligand.<sup>139</sup>



(XLV)

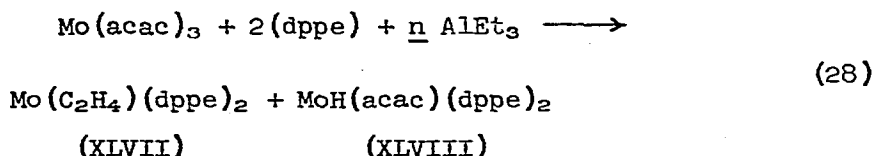
R = CH<sub>3</sub>

(XLVI)

(n = 1,2)

Reaction of either  $\text{NOPF}_6$  or  $\text{AgPF}_6$  with  $(\text{C}_6\text{Me}_{6-n}\text{H}_n)\text{Cr}(\text{CO})_2$  - (acetylene) ( $n = 0$  and  $1$ ; acetylene =  $\text{PhC}\equiv\text{CPh}$  and  $p\text{-MeOC}_6\text{H}_4\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{OMe}$ ) has been shown to afford the crystalline monocations  $[(\text{C}_6\text{Me}_{6-n}\text{H}_n)\text{Cr}(\text{CO})_2(\text{acetylene})]\text{PF}_6$ .<sup>140</sup> However when the acetylene is  $\text{MeCO}_2\text{C}\equiv\text{CCO}_2\text{Me}$  the reaction does not stop at the monocation acetylene derivative, instead further reaction with  $\text{NOPF}_6$  occurs with formation of  $[(\text{C}_6\text{Me}_5\text{H})\text{Cr}(\text{CO})_2(\text{NO})]\text{PF}_6$ . Cyclic voltammetry indicated that each acetylene complex underwent a reversible one-electron oxidation reaction followed by an irreversible electrochemical reaction (possibly loss of acetylene) at slightly more positive potentials. The monocationic acetylene complexes were also characterized by their room temperature ESR spectra in  $\text{CH}_2\text{Cl}_2$ .

The ratio of ethylene and hydrido products, XLVII and XLVIII respectively, depended on the value of  $n$  in eq 28.<sup>141</sup> With  $n > 5$ , (XLVII) was obtained exclusively in yields of 22%; with  $n = 2$  or  $3$ , (XLVIII) was obtained in 57% yield.



Metal-alkyl, -aryl, and -hydride complexes. New chemistry of complexes containing Group VIb metal to carbon sigma bonds is presented next. Methyl lithium reacts with molybdenum(II) acetate to yield  $\text{Li}_4[\text{Mo}_2\text{Me}_8] \cdot 4(\text{ether})$  (ether = THF,  $\text{Et}_2\text{O}$ , or dioxane) as bright red, pyrophoric crystals, readily soluble in ethers.<sup>142</sup> Reaction of the complexes with acetic acid regenerated  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ , with Mo-Mo bond intact. A crystal structure showed the octamethylmolybdenum tetraanion to be of  $D_{4h}$  symmetry

with none of the THF donor molecules co-axial to the Mo≡Mo bond.

Bis(trimethylsilyl)methyl has been employed as a ligand to stabilize  $\text{Cr}^{+3}$ .<sup>143</sup> The reaction product of  $\text{CrCl}_3$  with  $(\text{Me}_3\text{Si})_2\text{CHLi}$  in  $\text{Et}_2\text{O}$  was recrystallized from benzene and determined to be monomeric  $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3 \cdot \text{C}_6\text{H}_6$ . The compound was obtained as air-sensitive, paramagnetic (3.7 BM), bright-green crystals. The red diamagnetic species,  $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3 \cdot \text{NO}$  was prepared from  $\text{Cr}[\text{CH}(\text{SiMe}_3)_2]_3$  and NO.

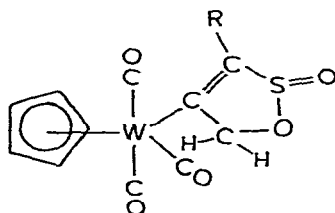
Autoxidation of hexakis(trimethylsilylmethyl)dimolybdenum(III), hexabenzoylditungsten(III) and hexaneopentylidimolybdenum(III) in hydrocarbon solvents at 20 and  $-74^\circ$  were found to proceed through a series of very rapid, free radical displacements at the metal center.<sup>144</sup> At  $-74^\circ$ , detection of the peroxy transition metal alkyls was possible however these reacted further with the alkyl to form the alkoxy compounds. Further studies of  $\sigma$ -bonded Cr(III)-C species illustrated the stability of  $(\text{H}_2\text{O})_5\text{CrCF}_3^{++}$  as compared to other Cr(III)-C complexes, towards aquation.<sup>145</sup> The intermediate monocation,  $(\text{H}_2\text{O})_4\text{CrCF}_3^+$ , was characterized and determined to accelerate the aquation reaction. The primary products of aquation,  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , HF and CO suggested difluorocarbene as an intermediate, leading to production of carbon monoxide in the acid aqueous medium.

Earlier studies of reductive cleavage of Co-C bonds in alkylcobaloxime complexes by  $\text{Cr}^{++}$  in aqueous solution to produce  $(\text{H}_2\text{O})_5\text{CrR}^{++}$  were extended to include reactions of the corrin complexes, methylcobalamin and ethylcobalamin.<sup>146</sup>

Stable  $\text{MeWOCl}_3$  and  $\text{MeWO}_2\text{Cl}$  complexes have been prepared in good yields from the reaction of  $\text{MeWCl}_5$  or  $\text{MeWOCl}_3$  (prepared from  $\text{WCl}_6$  and  $\text{Me}_2\text{Hg}$ ) with oxo-type ligands (i.e.,  $\text{OFR}_3$ ,  $\text{OAsPh}_3$  or  $\text{OSMe}_2$ ).<sup>147</sup>

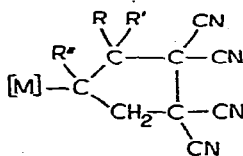


Another aspect of metal- $\sigma$ -carbon chemistry is illustrated by the following reports. The reaction of  $\text{CpMo}(\text{CO})_3\text{CH}_3$  with  $(\text{C}_6\text{H}_5)_3\text{As}$  in acetonitrile at  $35^\circ$  yielded the carbon monoxide insertion product  $\text{CpMo}(\text{COCH}_3)(\text{CO})_2\text{As}(\text{C}_6\text{H}_5)_3$ .<sup>148</sup> Kroll and Wojcicki have observed that  $\text{CpW}(\text{CO})_3\text{R}$  ( $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , and  $\text{CH}_2\text{C}_6\text{H}_5$ ) react with  $\text{SO}_2$  to afford stable complexes of the S-sulfinate,  $\text{CpW}(\text{CO})_3\text{S}(\text{O})_2\text{R}$ .<sup>149</sup> On the other hand,  $\text{CpW}(\text{CO})_3\text{CH}_2\text{C}\equiv\text{CR}$  ( $\text{R} = \text{CH}_3$  and  $\text{C}_6\text{H}_5$ ) was found to react with  $\text{SO}_2$  to yield the cycloaddition products  $\text{CpW}(\text{CO})_3\text{C}=\text{C}(\text{R})\text{S}(\text{O})\text{OCH}_2$  (XLIX). Desulfination of these complexes occurred upon contact with alumina.

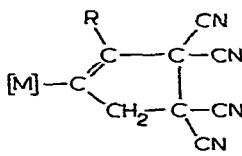


(XLIX)

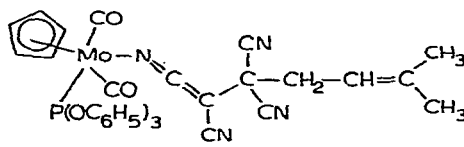
$\text{CpMo}(\text{CO})_3\text{CH}_2\text{CR}''=\text{CRR}'$  complexes have been found to react with tetracyanoethylene (TCNE) to yield the product derived by (3 + 2) cycloaddition with 1,2 metal migration (L);  $\text{CpMo}(\text{CO})_2(\text{L})-\text{CH}_2\text{C}\equiv\text{CR}$  ( $\text{L} = \text{CO}$  or  $\text{P}(\text{OC}_6\text{H}_5)_3$ ) affords complexes of the type (LI) upon treatment with TCNE.<sup>150</sup> In contrast,  $\text{CpMo}(\text{CO})_2[\text{P}(\text{OC}_6\text{H}_5)_3]-\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$  reacted slowly with TCNE to yield the ketenimato derivatives (LII). The reaction mechanism for the formation



(L)



(LI)



(LII)

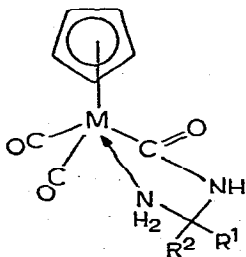
of these derivatives was discussed in terms of the intermediacy of dipolar metal-olefin and metal-allene complexes.

Pittman and Felis have carried out a detailed study of the synthesis and thermal decomposition reactions of  $(\eta^1\text{-C}_6\text{H}_5\text{CH}_2)\text{-}(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3$  ( $\text{M} = \text{Mo}$  and  $\text{W}$ ) and their polymer-bound analogs (linear and cross-linked polystyrenes).<sup>151</sup>

Only a few reports of new syntheses of VIb hydrido complexes were found in the 1974 literature. D'Aniello and Barefield have reported the synthesis of the first isolable hydrido complexes via the metal vaporization technique.<sup>152</sup> In this manner  $\text{Cp}_2\text{MH}_2$  ( $\text{M} = \text{Mo}, \text{W}$ ) were prepared by co-condensation of metal atom vapors and cyclopentadiene at  $-196^\circ$ .

The synthesis of tetrahydridotetrakis(methyldiphenylphosphine)-molybdenum(IV) from the reaction of  $\text{MoCl}_4(\text{PMePh}_2)_2$  (prepared from  $\text{MoCl}_4(\text{NCEt})_2$  and  $\text{MePh}_2\text{P}$  in  $\text{CH}_2\text{Cl}_2$ ) and  $\text{MePh}_2\text{P}$  and  $\text{NaBH}_4$  in ethanol has also been reported.<sup>153</sup>

The reaction of the metal hydride derivatives,  $\text{HM}(\text{CO})_3\text{Cp}$  ( $\text{M} = \text{Mo}$  and  $\text{W}$ ), with pentamethylene diaziridine has provided a new route to cyclic carbamoyl complexes (LIII).<sup>154</sup>



(LIII)

Finally, the presence of a  $\text{M-H}$  bond was proposed in the following work. Dimethylphenylphosphine reacts with  $\text{Cp}_2\text{M}(\text{CH}_2\text{CH}_2)\text{-Me}^+\text{PF}_6^-$  releasing ethylene and producing  $\text{Cp}_2\text{M}(\text{Me})(\text{PMe}_2\text{Ph})^+\text{PF}_6^-$

(M = Mo).<sup>155</sup> If however M = W, the product was proposed to contain a quaternary phosphonium ligand,  $[\text{Cp}_2\text{W}(\text{H})(\text{CH}_2\text{P}^+\text{Me}_2\text{Ph})]\text{PF}_6^-$ . In the trideuteriomethyl derivative,  $[\text{Cp}_2\text{W}(\text{C}_2\text{H}_4)\text{CD}_3]^+\text{PF}_6^-$ , the reaction product was found to be analogous to the Mo compound, i.e.,  $[\text{Cp}_2\text{W}(\text{CD}_3)_2\text{PMe}_2\text{Ph}]^+\text{PF}_6^-$ .<sup>156</sup> An equilibrium between intermediates of the type  $[\text{Cp}_2\text{WCH}_3]^+$  and  $[\text{Cp}_2\text{W}(=\text{CH}_2)\text{H}]^+$  is proposed to explain the results.

Metal-metal bonded complexes. This section on metal-metal bonded complexes is organized according to binding or interaction of the VIb metal with other metals according to the latter's family position in the periodic table. The reader may also refer to references 306, 307, and 346.

The structure and chemical properties of  $[\text{Cp}_2\text{Mo}(\text{H})\text{Mg}(\text{C}_6\text{H}_{11})-\mu\text{-Br}_2\text{Mg}(\text{Et}_2\text{O})_2]$ , containing a Mo-Mg bond and prepared by the reaction of  $\text{Cp}_2\text{MoH}_2$  with cyclohexylmagnesium bromide were presented.<sup>157</sup> The synthesis, characterization and structural properties of  $[\text{CpM}(\text{CO})_3\text{ZnCl}]_2$ , (M = Mo, W),  $[\text{CpM}(\text{CO})_3\text{ZnCl}\cdot\text{S}]_n$  (S =  $\text{Et}_2\text{O}$ , n = 2; S = 2,2'-dipy, n = 1) and  $[\text{CpM}(\text{CO})_3]_2\text{Zn}$  were also reported.<sup>158</sup>

An extensive series of reports dealing with VIb-Si compounds was published from Malisch's laboratory. The thermal stability of silyl complexes  $\text{CpM}(\text{CO})_3\text{SiR}_3$  (M = Mo, W; R = H,  $\text{CH}_3$ , Cl, Br), formed by reaction of the corresponding  $\text{Na}^+[\text{CpMo}(\text{CO})_3]^-$  with  $\text{R}_3\text{SiX}$  was found to depend highly on M, R, and, in solution studies, on solvent.<sup>159</sup> For example, the thermal decomposition proceeds with much more facility in THF than in  $\text{Et}_2\text{O}$  or hydrocarbon solvents, yielding as products  $[\text{CpM}(\text{CO})_3]_2$  and  $\text{R}_3\text{Si-O-SiR}_3$ . The facile halogenation of metal-substituted silicon hydrides such as  $\text{CpM}(\text{CO})_3\text{SiMe}_2\text{H}$ ,  $-\text{SiCl}_2\text{H}$ , etc., (M = Cr, Mo, W) by  $\text{CCl}_4$

and  $\text{CBr}_4$ , yielding the corresponding halo-silyl derivatives  $-\text{SiMeX}$ ,  $\text{SiCl}_2\text{X}$ , etc., was also studied by Malisch and Kuhn.<sup>160</sup> Other fluorine silyl metal compounds such as  $\text{CpM}(\text{CO})_3\text{SiMe}_{3-x}\text{F}_x$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) were described.<sup>161</sup>

$\text{Cp}(\text{CO})_3\text{WSiF}_3$ ,  $\text{Cp}(\text{CO})_3\text{MoSiCH}_3\text{F}_2$ ,  $\text{Cp}(\text{CO})_3\text{MoSiF}_3$ , and  $\text{Cp}(\text{CO})_3\text{CrSiCH}_3\text{F}_2$  have been found to react respectively with the phosphorus ylides  $(\text{CH}_3)_3\text{P}=\text{CHSi}(\text{CH}_3)_3$ ,  $(\text{C}_2\text{H}_5)_3\text{P}=\text{CHCH}_3$ ,  $(\text{CH}_3)_3\text{P}=\text{CH}_2$  and  $(\text{CH}_3)_3\text{P}=\text{CH}_2$  to yield the products  $(\text{CH}_3)_3\text{P}=\text{C}[\text{Si}(\text{CH}_3)_3]\text{SiF}_3$ ,  $[(\text{C}_2\text{H}_5)_3\text{P}-\text{CH}(\text{CH}_3)(\text{SiCH}_3\text{F}_2)][\text{Mo}(\text{CO})_3\text{Cp}]$ ,  $[(\text{CH}_3)_3\text{PCH}_2\text{SiF}_3][\text{Mo}(\text{CO})_3\text{Cp}]$ , and  $[(\text{CH}_3)_3\text{PCH}_2\text{SiCH}_3\text{F}_2][\text{Cr}(\text{CO})_3\text{Cp}]$ .<sup>162</sup>

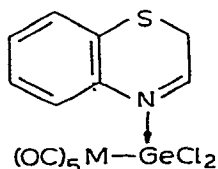
In yet another work Malisch prepared disilane transition metal complexes of the type  $\text{Cp}(\text{CO})_3\text{M}-\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_3$  and  $\text{Cp}(\text{CO})_3\text{M}-\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2\text{X}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) from the reaction of the anions  $[\text{Cp}(\text{CO})_3\text{M}]\text{Na}$  with the halodisilanes  $(\text{CH}_3)_5\text{Si}_2\text{X}$  or  $(\text{CH}_3)_4\text{Si}_2\text{X}_2$ .<sup>163</sup> The chlorodisilanyl complexes were converted into the fluorinated derivatives via reaction with  $\text{AgBF}_4$ . Reactions of these derivatives with ylides were investigated which resulted in metal  $\rightarrow$  carbanion transfer of the Si-Si group through metal-silicon bond cleavage and transylation.

Dossor, Eaborn, and Walton have studied base cleavage reactions of C-Si and C-Ge bonds in arenechromium tricarbonyl complexes and have found these reactions to occur much more readily than in the uncomplexed arene species.<sup>164</sup> Included in this study were the reactions of  $(\eta^6\text{-PhC}\equiv\text{CGeEt}_3)\text{Cr}(\text{CO})_3$ ,  $(\eta^6\text{-PhSiMe}_3)\text{Cr}(\text{CO})_3$ ,  $(\eta^6\text{-PhCH}_2\text{SiMe}_3)\text{Cr}(\text{CO})_3$ , as well as the corresponding free arenes, with a mixture of methanol (5 vol) and aqueous alkali (1 vol) at  $30^\circ$ .

Yamamoto and Todd have reported  $\sigma$ -bonded complexes of

some heteroatom boranes ( $1,2\text{-GeCHB}_{10}\text{H}_{10}^-$ ,  $7,8\text{-B}_9\text{H}_{10}\text{CHP}^-$ ,  $7,8\text{-B}_9\text{H}_{10}\text{As}_2^-$ ,  $\text{B}_{10}\text{H}_{12}\text{P}^-$  and  $\text{B}_{10}\text{H}_{12}\text{As}^-$ ) of the form  $(\pi\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{-GeCHB}_{10}\text{H}_{10}$  for example, which were prepared from reactions of the cationic complex  $(\pi\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3^+$  with the corresponding anions.<sup>165</sup> The borane ligand was proposed to be bound to the molybdenum atom by means of a  $\sigma$  bond through the germanium, phosphorus or arsenic atom.  $1,2\text{-B}_{10}\text{H}_{10}\text{CHGeM}(\text{CO})_5^-$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{and W}$ ) complexes have been prepared from the photochemical reaction of the corresponding hexacarbonyl with a 1/1 mole ratio of  $(\text{CH}_3)_4\text{N}[1,2\text{-B}_{10}\text{H}_{10}\text{CHGe}]$  in tetrahydrofuran.<sup>166</sup>

Chromium-, molybdenum-, and tungstenhexacarbonyl were shown to react with adducts of dichlorogermylene under photochemical conditions to yield the thermally quite stable, crystalline pentacarbonyl derivatives (LIV).<sup>167</sup> Trichlorogermidometalate complexes of chromium and molybdenum have also been prepared by Kruck and Molls.<sup>168</sup>



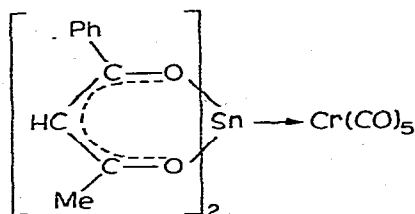
Several reactions using divalent tin halides resulted in the formation of  $\text{VIB-Sn}$  bonds.  $\text{M}(\text{CO})_5\text{SnX}_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}; \text{X} = \text{Cl}, \text{Br}, \text{I}$ ) complexes have been prepared by photolysis of  $\text{M}(\text{CO})_6$  and  $\text{SnX}_2$  in THF.<sup>169</sup> Similarly,  $\text{M}(\text{CO})_5\text{GeCl}_2$  was synthesized from  $\text{M}(\text{CO})_6$  and  $\text{CsGeCl}_3$ . Reactions of these neutral species with  $\text{Me}_4\text{NX}$  in THF produced the anions  $[\text{M}(\text{CO})_5\text{SnX}_3]^-$  and  $[\text{M}(\text{CO})_5\text{GeCl}_3]^-$ . The tetrahydrofuran adduct of

$(t\text{-Bu})_2\text{SnCr}(\text{CO})_5$  was ranked in a series of Group IVa and IVb Lewis acids according to the strength of their interaction with aliphatic nitroxides as determined by epr.<sup>170</sup>

$[\text{CpCr}(\text{CO})_3]_2\text{SnX}_2$  (X = Cl and Br) have been prepared from the reaction of  $\text{Et}_4\text{N}[\text{CpCr}(\text{CO})_3]$  with  $\text{SnX}_2$  in acetone in yields of 26-48%. A relatively strong Cr-Sn bond is indicated by ir and mass spectral measurements.<sup>171</sup>

An investigation of reactions of tin(II) halides with a variety of compounds containing transition metal-carbon  $\sigma$  bonds has been carried out by Cole, Cotton, and McWilliam.<sup>172</sup> Although no reaction between  $\text{CpMo}(\text{CO})_3\text{CH}_3$  and  $\text{SnCl}_2$  in refluxing methanol was detected, under uv irradiation a reaction occurred producing  $\text{CpMo}(\text{CO})_3\text{SnCl}_3$  and subsequently  $\text{Cl}_2\text{Sn}[\text{Mo}(\text{CO})_3\text{Cp}]_2$ . Similarly no insertion compound was observed with  $\text{SnBr}_2$ .

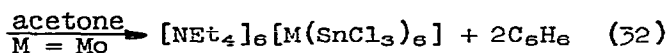
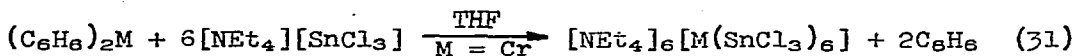
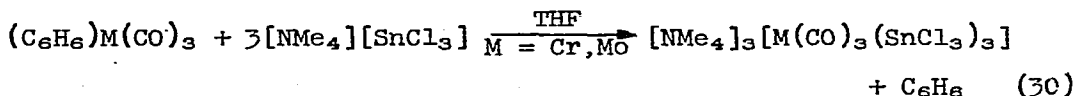
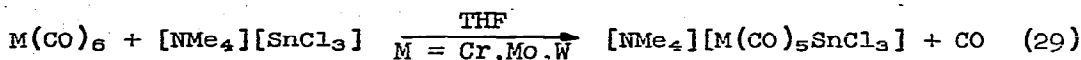
Complexes containing divalent tin ligands such as  $(\text{C}_5\text{H}_5)_2\text{SnW}(\text{CO})_5$  and (LV), have been isolated as brown and pale yellow powders respectively from the photolysis of  $\text{M}(\text{CO})_6$  and the corresponding divalent tin ligands.<sup>173</sup>



(LV)

Reaction of  $\text{M}(\text{CO})_6$  (M = Cr, Mo, W) with  $\text{Et}_4\text{N}[\text{SnBr}_{3-n}\text{Cl}_n]$  (n = 0-2) photochemically in  $\text{CH}_2\text{Cl}_2$  or thermally in refluxing THF gave complexes containing M-Sn bonds of the type  $\text{Et}_4\text{N}[\text{M}(\text{CO})_5\text{SnBr}_{3-n}\text{Cl}_n]$ .<sup>174</sup> In addition,  $[\text{Et}_4\text{N}]_6[\text{Cr}(\text{SnBr}_{3-n}\text{Cl}_n)_6]$  (n = 1 and 2) complexes were prepared from  $(\text{C}_6\text{H}_6)_2\text{Cr}$  and

$\text{Et}_4\text{N}[\text{SnBr}_{3-n}\text{Cl}_n]$  in refluxing THF. Similar reactions with trichlorotin salts yielded the derivatives shown as products in equations 29 through 32.<sup>175</sup> All products were isolable, crystalline salts.

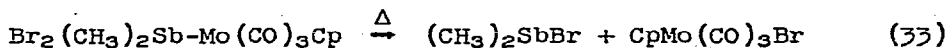


The preparation and properties of other compounds containing molybdenum-tin bonds,  $(\text{CO})_2(\text{C}_7\text{H}_7)\text{MoSnPh}_n\text{Cl}_{3-n}$  ( $n = 0, 1, 2,$  and  $3$ ) and  $(\text{CO})_2(\text{C}_7\text{H}_7)\text{MoSnBr}_3$ , were also reported.<sup>176</sup>

The reactions of  $(\text{CH}_3)_3\text{SnCH}_2\text{I}$  with the sodium salts of a variety of metal carbonyl anions have been shown by King and Hodges to result in cleavage of a carbon-tin bond to give mixtures of the trimethyl tin and methyl derivatives.<sup>177</sup> Included in this study was the reaction of  $(\text{CH}_3)_3\text{SnCH}_2\text{I}$  with  $\text{NaMo}(\text{CO})_3\text{Cp}$  to yield  $(\text{CH}_3)_3\text{SnMo}(\text{CO})_3\text{Cp}$  and  $\text{CH}_3\text{Mo}(\text{CO})_3\text{Cp}$ . The latter derivative was proposed to arise from reaction of the unstable " $\text{NaCH}_2\text{I}$ " species and the metal carbonyl anion followed by solvent protonation.

$\text{Na}[\text{CpM}(\text{CO})_3]$  ( $\text{M} = \text{Cr, Mo, W}$ ) was found to react with  $\text{BrSb}(\text{CH}_3)_2$  to yield  $\text{CpM}(\text{CO})_3\text{Sb}(\text{CH}_3)_2$  derivatives.<sup>178</sup> Further reactions of these derivatives with  $(\text{CO})_5\text{W}(\text{THF})$  or  $(\text{CO})_4\text{W}(\text{norbornadiene})$  yielded  $\text{Cp}(\text{CO})_3\text{MSb}(\text{CH}_3)_2\text{-W}(\text{CO})_5$  or

$[\text{Cp}(\text{CO})_3\text{MSb}(\text{CH}_3)_2]_2\text{W}(\text{CO})_4$ , respectively. The reactions of  $[\text{CpM}(\text{CO})_3\text{Sb}(\text{CH}_3)_2]$  with  $(\text{CH}_3)_2\text{P}=\text{CHR}$  ( $\text{R} = \text{H}, \text{Si}(\text{CH}_3)_3$ ) and  $\text{RB}^-$  ( $\text{R} = \text{CH}_3, \text{CH}_2 = \text{CHCH}_2, \text{C}_6\text{H}_5\text{CH}_2$ ) were also described. The analogous metal substituted arsanes such as  $\text{CpM}(\text{CO})_3\text{As}(\text{CH}_3)_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ), prepared by reaction of  $\text{CpM}(\text{CO})_3^- \text{Na}^+$  or  $\text{CpM}(\text{CO})_3\text{Si}(\text{CH}_3)_3$  with  $(\text{CH}_3)_2\text{AsCl}$ , readily quaternize with, e.g.,  $\text{CH}_3\text{I}$ , yielding salts such as  $[\text{CpCr}(\text{CO})_3\text{As}(\text{CH}_3)_3]^+ \text{I}^-$ .<sup>179</sup> The corresponding antimony compounds,  $\text{CpM}(\text{CO})_3\text{Sb}(\text{CH}_3)_2$  also add  $\text{Br}_2$  to become Sb(V) derivatives whose chemical behavior is determined by the tendency of the Sb to acquire tri-coordination (eq 33).<sup>180</sup>



The metal-metal bonded molybdenum dimer  $[\text{CpMo}(\text{CO})_3]_2$  has been observed to undergo light catalyzed substitution and disproportionation reactions with  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{SCN}^-$  to yield  $\text{CpMo}(\text{CO})_3^-$ ,  $\text{CpMo}(\text{CO})_3\text{X}$ , and  $\text{CpMo}(\text{CO})_2\text{X}_2^-$ .<sup>181</sup> The latter species was shown to result from a second light-catalyzed displacement of CO from  $\text{CpMo}(\text{CO})_3\text{X}$ . Quantum yield measurements on the reaction of the dimer with  $\text{Br}^-$  in acetone were very wavelength dependent.  $\Phi_{546}$  and  $\Phi_{366}$  were observed to be  $0.36 \pm 0.06$  and  $0.07 \pm 0.02$ , respectively. The quantum efficiencies of these photoreactions of  $[\text{CpMo}(\text{CO})_3]_2$  with  $\text{X}^-$  were all found to be strongly solvent dependent with acetone, tetrahydrofuran, and acetonitrile being of much higher efficiency than benzene. The marked facility of  $[\text{CpCr}(\text{CO})_3]_2$  metal-metal bond cleavage using reagents such as Cd, Hg,  $\text{HgCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ , and  $\text{I}_2$  was also noted.<sup>182</sup> Carbonyl displacement in both the dimer and the iodo-cleaved product,  $\text{CpCr}(\text{CO})_3\text{I}$ , by  $\text{PR}_3$  ligands proceeds readily in refluxing EtOH or pentane.



Reaction of  $\text{Mo}(\text{CO})_6$  or  $\text{Fe}_2(\text{CO})_9$  with  $\text{Na}_2[\text{Cr}(\text{CO})_5]$  affords the mixed dinuclear carbonylmetalates  $\text{Na}_2[(\text{OC})_5\text{Cr}-\text{Mo}(\text{CO})_5]$  and  $\text{Na}_2[(\text{OC})_5\text{Cr}-\text{Fe}(\text{CO})_4]$  derivatives, respectively.<sup>183</sup>

Molecular nitrogen and nitrosyl complexes. A review of the first seven years' work in determining the synthesis, properties and significance of transition metal dinitrogen complexes also explored their role as potential intermediates of  $\text{N}_2$  assimilation.<sup>184</sup> Some 86 references are given.

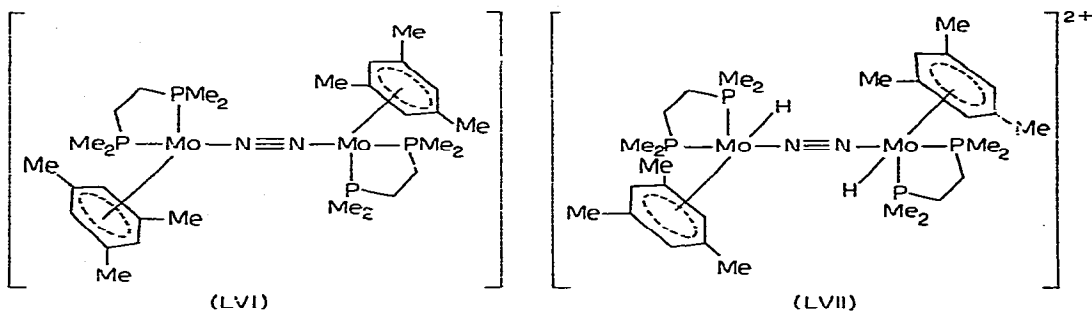
A low-yield abiological fixation of Mo-bound  $\text{N}_2$  was reported by van Tamelen and co-workers,<sup>185</sup> utilizing trans-(dppe)<sub>2</sub>Mo( $\text{N}_2$ )<sub>2</sub> and the 4Fe-4S cluster compounds,  $\text{Fe}_4\text{S}_4(\text{SEt})_4^{n-}$ ,  $n = 2, 3, 4$ ; however a reinvestigation of this reaction of trans-[Mo( $\text{N}_2$ )<sub>2</sub> - (dppe)<sub>2</sub>] with HCl in the presence of  $[\text{Fe}_4\text{S}_4(\text{SEt})_4]^{2-}$  showed no  $\text{NH}_3$  as products but rather  $[\text{MoCl}_2(\text{dppe})_2]^+$ ,  $\text{H}_2\text{S}$ , EtSH,  $\text{H}_2$ , iron chlorides, and  $\text{N}_2$ .<sup>186</sup> On the other hand, the reduction of dinitrogen at a monometal site was observed in studies of the reactions of [trans-M( $\text{N}_2$ )<sub>2</sub>(diphos)<sub>2</sub>] (diphos = dppe or depe,  $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ ) and cis-W( $\text{N}_2$ )<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>4</sub> with hydrogen halides.<sup>187</sup> During this work the following compounds were obtained and characterized:  $[\text{MX}_2(\text{N}_2\text{H}_2)\text{dppe}_2]$ ,  $\text{Mo}(\text{N}_2\text{H}_2)\text{depe}_2\text{X}$ , trans-[WCl( $\text{N}_2\text{H}_2$ )-PMe<sub>2</sub>Ph)<sub>4</sub>]Cl, and  $[\text{WH}(\text{N}_2)_2\text{dppe}_2]\text{HCl}_2$ .

In another  $\text{N}_2$ -fixation related work, Shilov and co-workers have pointed out that ATP has no specific stimulating effect over ADP towards molybdenum/glutathione reduction of acetylene when the two reagents are added in solutions of equal pH.<sup>188</sup> A further contribution to nitrogenase model systems was based on dimeric molybdenum(V) N,N-dialkyldithiocarbamates.<sup>189</sup>

The preparation of trans-[Mo( $\text{N}_2$ )<sub>2</sub>(dppe)<sub>2</sub>] from Mo(acac)<sub>3</sub> and dppe in the presence of  $\text{AlEt}_3$  has been reported in detail.<sup>190</sup>

In a similar report the complexes  $\text{MoH}(\text{acac})(\text{dppe})_2$  ( $\text{acac} =$  pentane-2,4-dionato) and  $\text{Mo}(\text{C}_2\text{H}_4)(\text{dppe})_2$  were prepared by reaction of  $\text{Mo}(\text{acac})_3$  with  $\text{AlEt}_3$  in the presence of  $\text{dppe}$ .<sup>191</sup> (See ref. 141 also.) Ethylene may be reversibly replaced in  $\text{Mo}(\text{C}_2\text{H}_4)(\text{dppe})_2$  by two molecules of  $\text{N}_2$  forming trans- $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ . Sodium may also be used as a reducing agent in these preparations. Thus,  $\text{Mo}(\text{dppe})_2(\text{N}_2)\text{Cl}$  as well as  $\text{Mo}(\text{dppe})_2(\text{N}_2)_2$  were prepared by the sodium reduction of  $\text{Mo}_2(\text{dppe})_2\text{Cl}_6 \cdot 2\text{C}_6\text{H}_6$  in the presence of  $\text{dppe}$ .<sup>192</sup>

Treatment of the dinitrogen complex (LVI) with tetrafluoroboric acid yielded the dication (LVII).<sup>193</sup>



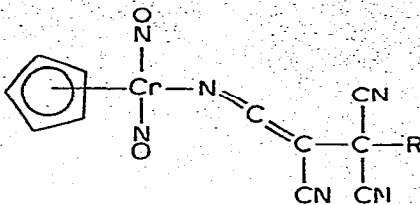
The cis- $\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$  complex was used as precursor of a ligating carbon dioxide complex,  $\text{Mo}(\text{CO}_2)_2(\text{PMe}_2\text{Ph})_4$ , which seemingly disproportionates (or reacts with  $\text{O}_2$ ) in solution to yield the carbonato-bridged complex,  $(\text{PhMe}_2\text{P})_3(\text{CO})\text{Mo}(\mu\text{-CO}_3)_2\text{Mo}(\text{CO})(\text{PMe}_2\text{Ph})_3$ .<sup>194</sup> The latter was characterized by X-ray crystallography.

The preparation and properties of several new nitrosyl complexes were reported. Reductive nitrosation of  $\text{MoCl}_5$  with  $\text{NO}$  in the presence of  $\text{PPh}_3$  in methylene chloride has been observed to afford  $\text{Mo}(\text{NO})\text{Cl}_3(\text{OPPh}_3)_2$  as an intermediate with

eventual formation of  $\text{Mo}(\text{NO})_2\text{Cl}_2(\text{OPPh}_3)_2$  as a final product.<sup>195</sup> The final product existed as the bis-benzene solvated derivative when the reaction was run in benzene solution. Another dichloro-dinitrosylmolybdenum complex was also reported.<sup>196</sup> In addition, an interesting thionitrosyl complex,  $[\text{Mo}(\text{NS})(\text{S}_2\text{CNR}_2)_3]$  was also prepared.<sup>197</sup>

Chromium nitrosyl complexes have been prepared by way of electrochemical reduction of various Cr(III) complexes such as  $\text{Cr}(\text{CN})_6^{3-}$  in the presence of nitrite ion.<sup>198</sup> In yet another nitrosyl complex preparation, Stewart has prepared  $[\text{CpW}(\text{NO})_2\text{CO}]\text{PF}_6$  as a green solid in  $\sim 90\%$  yield from the reaction of  $\text{NOPF}_6$  and  $\text{CpW}(\text{CO})_2\text{NO}$  in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  at  $-78^\circ$ .<sup>199</sup> The lability of the carbonyl ligand in this complex offered a convenient route to a variety of cationic and neutral nitrosyl derivatives, including  $[\text{CpW}(\text{NO})_2\text{L}]\text{PF}_6$  (L = tertiary phosphine, arsine or stibine) and  $\text{CpW}(\text{NO})_2\text{X}$  (X = Cl, Br, I).

Several reactions of nitrosyl complexes were studied. The oxidative addition of halogens to nitrosyl and arylazo derivatives of Mo and W, namely  $(\text{HBPz}_3)\text{M}(\text{CO})_2\text{NO}$  and  $(\text{HBPz}_3)\text{-M}(\text{CO})_2\text{N}_2\text{Ph}$  (Pz = 1-pyrazolyl), has been investigated by Deane and Lalor.<sup>200</sup> A variety of products were observed including those containing bridging  $\text{ArN}_2$  ligands and an  $\text{ArN}_2^-$  derivative. Hanna and Wojcicki have carried out a study of reactions between  $\text{CpCr}(\text{NO})_2\text{R}$  (R =  $\text{CH}_3$ ,  $\text{CH}_2\text{C}_6\text{H}_5$ ) with CO, SCO,  $\text{SO}_2$ , and TCNE.<sup>201</sup> Whereas  $\text{SO}_2$  readily inserts into the Cr- $\text{CH}_3$  bond to yield stable S-sulfinato complexes,  $\text{CpCr}(\text{NO})_2\text{S}(\text{O})_2\text{R}$ , CO and SCO are not reactive in these systems. Tetracyanoethylene was found to react with  $\text{CpCr}(\text{NO})_2\text{CH}_3$  to afford  $\text{CpCr}(\text{NO})_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{CH}_3$  and with  $\text{CpCr}(\text{NO})_2\text{CH}_2\text{C}_6\text{H}_5$  to yield both  $\text{CpCr}(\text{NO})_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{-CH}_2\text{C}_6\text{H}_5$  and  $\text{CpCr}(\text{NO})_2\text{N}=\text{C}=\text{C}(\text{CN})\text{C}(\text{CN})_2\text{CH}_2\text{C}_6\text{H}_5$  (LVIII).



Isocyanide derivatives of Group VIb nitrosyls were the subjects of two reports. The syntheses of trans- $W(CO)_4(NO)X$  ( $X = Cl, I$ ) via cleavage of  $HW_2(CO)_9NO$  by  $NOCl$  or  $I_2$  were presented by King and co-workers.<sup>202</sup> Tert-butyliisocyanide complexes such as  $[(CH_3)_3CNC]_xW(CO)_{4-x}(NO)X$  ( $x = 1-4$ ) may be readily obtained by thermal displacement of CO ligands. The isocyanide complexes,  $[CpMo(NO)X_2(CNR)]$  ( $X = Br$  or  $I$ ),  $[Mo(NO)(CNR)_5]X$  ( $X = I$  or  $PF_6$ ) and  $[Mo(NO)(CNR)_4I]$ , have been prepared from the reaction of  $[CpMo(NO)X_2]_2$  with  $CNR$  ( $R =$  alkyl).<sup>203</sup> Treatment of  $[Mo(NO)(CNR)_5]I$  with  $R'NH_2$  afforded  $[Mo(NO)(CNR)_4\{C(NHR)(NHR')\}]I$  or  $[Mo(NO)(CNR)_4(NH_2R')]I$  ( $R' =$  alkyl) depending on temperature.

Miscellaneous complexes and methods. A new high yield preparation of  $Cr(CO)_6$  utilized the reduction of  $CrCl_3 \cdot 3THF$  in benzene with potassium in the presence of KI followed by reaction with CO (autoclave at 280 atm) at  $220^\circ C$  for 16-20 hours.<sup>204</sup> An additional synthesis of  $Cr(CO)_6$  was carried out using activated magnesium (prepared via reduction of  $MgCl_2$  with potassium/KI) which afforded an even greater yield of 83%.

A facile route to the production of  $M(CO)_5^-$  in ca. 95% yield for  $M = Cr$  and in much poorer yields for  $M = Mo$  and  $W$ , utilizes Na dissolved in HMPA.<sup>205</sup> The  $Cr_2(CO)_{10}^{2-}$  ion is shown to be intermediate in the reduction reaction as well as the

product when trace amounts of  $O_2$  are added to  $Cr(CO)_5^{2-}$ . Discrepancies with the earlier literature are accounted for by this extreme air sensitivity of the mononuclear dianions.

Douglas and Ruff have succeeded in preparing the anions  $[M(CO)_5F]^-$  where  $M = Cr, W$ .<sup>208</sup> Of the two procedures employed, photochemical reaction of  $M(CO)_6$  with  $[(C_6H_5)_3P]_2NF$  in  $CH_2Cl_2$  and reaction of  $AgF$  with  $M_2(CO)_{10}^{2-}$ , the former gave much higher yields.

Wentworth and co-workers further defined the use of metal carbonyl derivatives in the synthesis of di- or trinuclear molybdenum halide anions. Thus, salts of  $Mo_2Cl_9^{3-}$  and  $Mo_2Br_9^{3-}$  were synthesized in high yields by way of the halopentacarbonylmolybdenum anions (eqs 34 and 35).<sup>207</sup> In addition, salts of



$Mo_2Cl_9^{3-}$ ,  $Mo_2Cl_9^{2-}$ , and  $Mo_3Cl_{12}^{3-}$  were also prepared by the oxidative displacement of CO from  $Mo(CO)_4Cl_3^-$ , specifically by reaction with  $MoCl_6^{2-}$ ,  $MoCl_6^-$ , or with  $Mo_2Cl_9^{2-}$  (to yield trinuclear  $Mo_3Cl_{12}^{3-}$ ).<sup>208</sup>

The VIb metal carbonyls were used as metal source in the preparation of tris(o-tetrachlorobenzoquinone)chromium, molybdenum, and tungsten.<sup>209</sup> Simple reflux in benzene of the two reagents,  $M(CO)_6$  and the benzoquinone, gave the desired products.  $(PhNC)_5CrL$  (L = dimethyl fumarate and fumaronitrile) complexes have been prepared via photolysis of  $(PhNC)_6Cr$  in the presence of L.<sup>210</sup>

The dithiocarbamate complexes  $MoO_2(S_2CNR_2)_2$  have been found to react with phenylhydrazine and  $NaS_2CNR_2$  to give brown

air-stable phenylazo complexes of the form  $[\text{Ph-N=N-Mo}(\text{S}_2\text{CNR}_2)_3]$ . Methylazo and benzoylazo complexes were obtained in an analogous manner. However, the oxime complex  $\text{MoO}_2(\text{C}_6\text{H}_5\text{NO})_2$  and phenylhydrazine reacted to give the bis(phenylazo) complex,  $\text{Mo}(\text{N}_2\text{Ph})_2(\text{C}_6\text{H}_5\text{NO})_2$ . On the other hand, 1,1-dimethylhydrazine was shown to react with  $\text{MoO}_2\text{L}_2$  (L = oxime or dithiocarbamate) to give the N,N-dimethylhydrazido-N'(2-)oxo complexes  $\text{MoO}(\text{NNMe}_2)\text{L}_2$ . Alkylation and protonation reactions of these azo complexes were also carried out.<sup>211</sup>

Cyclic voltammetry studies prompted the electrochemical synthesis of  $\text{Cr}(\text{CO})_6^+$ . The 17-electron species thus produced in  $\text{MeCN-Bu}_4\text{NBF}_4$  at a Pt electrode displayed an esr signal which grew with time of electrolysis and decayed by a second order process.<sup>212</sup> The electrochemical oxidation and reduction of complexes of  $[\text{M}(\text{CO})_2(\text{dppe})_2]^{0,+1,+2}$  (M = Mn, Mo, W, Cr) were carried out in order to determine the effect of oxidation state on stereochemistry.<sup>213</sup> Trans isomers are favored at higher oxidation states; the electrochemically produced cis isomers of  $\text{M}(\text{CO})_2(\text{dppe})_2^+$  (M = Cr, Mo, W) readily isomerize to the trans form.

Reactions of low valent transition metal complexes, including Group VIb carbonyls and substituted carbonyl complexes, with the Karl Fischer reagent (pyridine,  $\text{SO}_2$  and  $\text{I}_2$ ) resulting in oxidation of the metal have been described.<sup>214</sup> Corey and Fleet have employed the chromium trioxide-3,5-dimethylpyrazole complex as a reagent for the oxidation of alcohols to carbonyl compounds.<sup>215</sup>

Greco and co-workers have reported the reactions of W(VI) and Mo(V) chlorides with azoxybenzene to yield ionic products

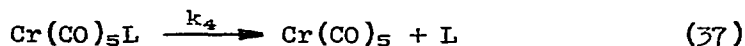
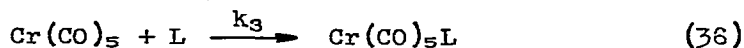
of W(VI) and Mo(VI) oxychlorides where the cation is a protonated azobenzene.<sup>216</sup> In addition, the reaction of MoCl<sub>5</sub> or MoOCl<sub>4</sub> and azoxybenzene afforded the complex [trans-MoOCl<sub>4</sub> · (OC<sub>2</sub>H<sub>5</sub>)]<sup>-</sup> [C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>H]<sup>+</sup>. Several complexes of substituted azoxybenzene were also described.

The molybdenum complex Mo(CO)<sub>4</sub>L (L = [p-RC<sub>6</sub>H<sub>4</sub>(p-R<sup>1</sup>C<sub>6</sub>H<sub>4</sub>N:)C]<sub>2</sub>) has been prepared via reaction of Mo(CO)<sub>6</sub> with L in refluxing C<sub>6</sub>H<sub>6</sub>.<sup>217</sup> Further CO substitution with PR<sub>3</sub><sup>2</sup> to yield Mo(CO)<sub>3</sub>L(PR<sub>3</sub><sup>2</sup>) derivatives was also reported.

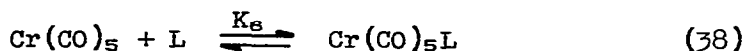
### Kinetic and Mechanistic Studies

Many mechanistic studies of fluxional molecules are included under the nmr section of Spectroscopic Studies. The work presented here deals primarily with ligand exchange and isomerization, and with reactions at σ- or π-bonded carbon to metal sites.

The rates of reaction of Cr(CO)<sub>5</sub> with several solvents (eq 36) and of the decay of the Cr(CO)<sub>5</sub>L species in CO-saturated cyclohexane solutions (eq 37) have been determined by both conventional and laser flash photolysis.<sup>218</sup>



From the values of k<sub>3</sub> and k<sub>4</sub> the equilibrium constant for the process shown in eq 38 was computed to give a measure of the stability of the Cr(CO)<sub>5</sub>L complex. The rate constant



k<sub>3</sub> was found to increase in the order: benzene (7.0 × 10<sup>6</sup> M<sup>-1</sup>·s<sup>-1</sup>).

$\text{sec}^{-1}) < \text{diethyl ether} < \text{methanol} < \text{ethyl acetate} < \text{acetone} < \text{acetonitrile}$  ( $1.6 \times 10^8 \text{ M}^{-1}\text{-sec}^{-1}$ ).  $k_4$  was found to increase in the reverse order. Similarly, the stability of the complex  $\text{Cr}(\text{CO})_5\text{L}$  (given by  $K_6$ ) also increased in the order: benzene, diethyl ether, ethyl acetate, acetone, and acetonitrile. The rate and equilibrium parameters were suggested as possible solvent parameters for organometallic reactions (e.g., the catalytic oligomerization of butadiene by dibutadieneiron monocarbonyl).

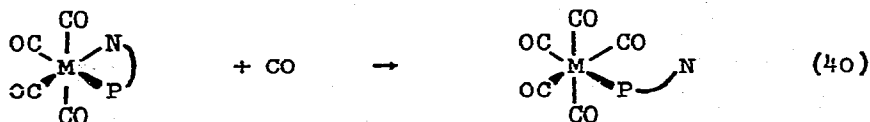
Dobson has reexamined the system illustrated by eq 39



(A = amine, L = heavier Group V Lewis base) and found that the previously reported  $K_{\text{eq}}$  temperature dependences and the corresponding thermodynamic parameters were erroneous in that the time requirement to achieve equilibrium was much longer than that assumed by the earlier workers.<sup>219</sup>

The chelate complexes,  $\text{Mo}(\text{CO})_4[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]$  and cis- $\text{Mo}(\text{CO})_3[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]$ , have been found to react with  $^{13}\text{CO}$  with replacement of the N-donor site to yield stereospecifically cis  $^{13}\text{CO}$  species.<sup>220</sup>

Further kinetic investigations of the chelate ring-opening represented below as dependent on the chelate ligand structure was described by Angelici.<sup>221</sup> The reaction rate is first order



in both complex and CO concentration, and for the series  $\text{Mo}(\text{CO})_4(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{NR}_2)$  ( $n = 2$ ), the rates increase with bulki-

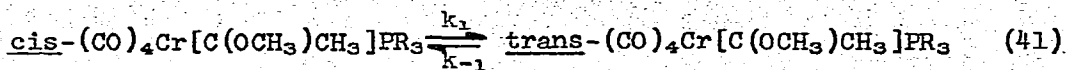


ness of the  $\text{NR}_2$  donor group. Rates of product formation also increase with increasing values of  $n$  both for the  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{NMe}_2$  ligand as well as the pyridylphosphine derivatives,  $\text{Ph}_2\text{P}(\text{CH}_2)_n - \text{C}_5\text{H}_4\text{N}$ .<sup>222</sup> A similar ring-opening mechanism is proposed in both studies.

Connor and Hudson have measured rate data and activation parameters for the ring-closure reactions of  $\text{Mo}(\text{CO})_5(\text{dppe})$  and of  $\text{Mo}(\text{CO})_5(\text{dmpe})$  ( $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ) to give cis- $\text{Mo}(\text{CO})_4(\text{dppe})$  and cis- $\text{Mo}(\text{CO})_4(\text{dmpe})$ , respectively.<sup>223</sup> The rate of dppe closure was approximately twice as fast as that of the dmpe analog. These reactions were observed to proceed more rapidly than their chromium counterparts. In addition, these workers report the preparation and properties of the chelate-bridged hetero-metallic complex  $(\text{CO})_5\text{Mo}(\text{dmpe})\text{Mn}(\text{CO})_4\text{Br}$ .

Dobson and co-workers have investigated the kinetics and mechanism of reactions of the Group VIb metal hexacarbonyls with tetrabutylammonium halides in chlorobenzene to afford  $\text{Bu}_4\text{N}[\text{M}(\text{CO})_5\text{X}]$  products.<sup>224</sup> These reactions were shown to obey the second-order rate law,  $\text{rate} = k_2[\text{M}(\text{CO})_6][\text{Bu}_4\text{NX}]$ , for  $\text{M} = \text{Mo}$  and  $\text{W}$ . However, for  $\text{M} = \text{Cr}$ , an additional ligand independent term in the rate law was observed,  $\text{rate} = k_1[\text{Cr}(\text{CO})_6] + k_2[\text{Cr}(\text{CO})_6][\text{Bu}_4\text{NX}]$ . The steric nature of the halide was influential on the rate of the reaction with  $\text{Cl} > \text{Br} > \text{I}$ . These observations taken together were suggestive of the second-order path involving attack of the halide at the metal center for  $\text{Mo}$  and  $\text{W}$  but at a carbonyl carbon atom for  $\text{Cr}$ .

Fischer, Fischer and Werner have studied the kinetics of the isomerization reactions (eq 41) of  $(\text{CO})_4\text{Cr}[\text{C}(\text{OCH}_3)\text{CH}_3]\text{PR}_3$  ( $\text{R} = \text{C}_2\text{H}_5$  and  $\text{C}_6\text{H}_{11}$ ) in methylcyclohexane and toluene.<sup>225</sup> The



(A)

(B)

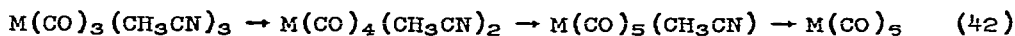
isomerization process obeys a first-order rate law of the form  $\text{rate} = k_1[\text{A}] - k_{-1}[\text{B}]$ , where excess phosphine or carbon monoxide have no significant effect on the rate of interconversion. Phosphine exchange studies also indicated that the isomerization takes place via neither a phosphine nor a CO bond cleavage. The  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values were obtained for both the forward and reverse reactions for both phosphines and solvent and their respective ranges were 21.2 to 25.7 kcal/mol and -6.5 to +5.0 e.v. These results were discussed in terms of a trigonal twist intramolecular isomerization process.

Photochemical reaction studies of  $\text{M}(\text{CO})_5\text{L}$  suggested simultaneous L and CO photodissociation in the 366-439 nm region with a predominance of L substitution over the entire irradiation range.<sup>226</sup>

The photochemical exchange of  $^{13}\text{CO}$  for  $^{12}\text{CO}$  in (norbornadiene) $\text{M}(\text{CO})_4$  (M = Cr, Mo, W) resulted in stereospecific enrichment of axial sites.<sup>227</sup> Thermal equilibration of axial and equatorial sites was interpreted in terms of a metal olefin bond opening and subsequent rearrangement of the 5-coordinate intermediate.

Proton nmr spectra were used to monitor the exchange of  $\text{CD}_3\text{CN}$  for  $\text{CH}_3\text{CN}$  in the nitrosyl complexes,  $\text{cis}-[\text{M}(\text{NO})_2(\text{CH}_3\text{CN})_4]^{2+}$ , M = Mo and W.<sup>228</sup> The exchange half-life was independent of  $\text{CD}_3\text{CN}$  concentration and the complex stereospecifically exchanged only two  $\text{CH}_3\text{CN}$  molecules, supposedly those trans to the NO ligands. A dissociative pathway and stereochemical rigidity of the resultant 5-coordinate intermediate was proposed.

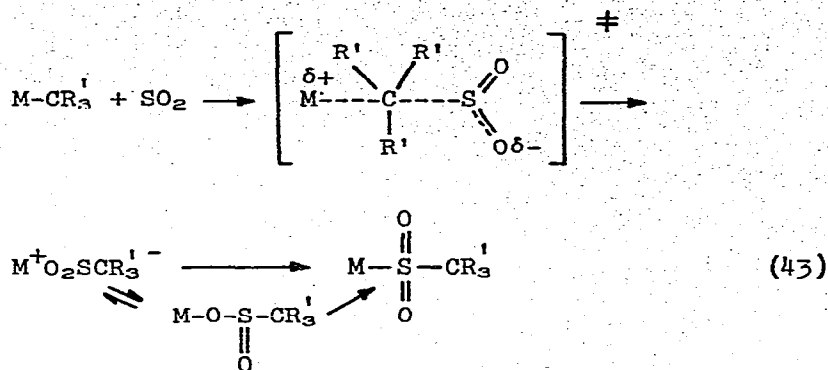
Graham and Kilner have studied disproportionation reactions (eq 42) of  $[M(CO)_{6-n}(CH_3CN)_n]$  ( $M = Cr, Mo, W; n = 1-3$ ) complexes.<sup>229</sup> These processes were shown to occur rapidly in Nujol and acetone solvents at room temperature but only at much higher temperatures in acetonitrile solution. The CO necessary in forming less-substituted derivatives is derived from CO produced by decomposition of the more highly substituted species. The nature of an intermediate possessing a strong  $\nu(CO)$  absorption at  $1996\text{ cm}^{-1}$  was proposed to be trans- $W(CO)_4(CH_3CN)_2$ . This however appears unlikely because of the high frequency of the observed vibration.



Barnett and Pollmann have investigated the kinetics of the decarbonylation reaction of trans- $CpMo(CO)_2(L)COCH_3$  where L is a variety of tertiary phosphines.<sup>230</sup> The observed order of reactivity was found to correlate with the steric bulk of the phosphine ligand. At  $60^\circ$  in acetonitrile the sequence of relative rates observed was  $P(c-C_6H_{11})_3 > P(C_6H_5)_2(i-C_3H_7) > P(C_6H_5)_3 > P(p-CH_3C_6H_4)_3 > P(p-CH_3OC_6H_4)_3 > P(C_6H_5)_2CH_3 > P(i-C_4H_9)_3 > P(C_6H_5)(CH_3)_2 \gg P(n-C_4H_9)_3$ .  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for this process was found to be 29.3(30.3) and 4.2(7.4) for  $P(C_6H_5)_3$  (and  $P(n-C_4H_9)_3$ ), respectively, suggesting CO dissociation as rate determining.

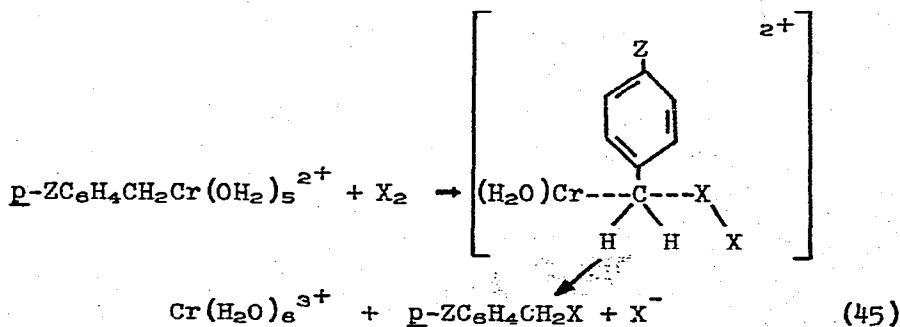
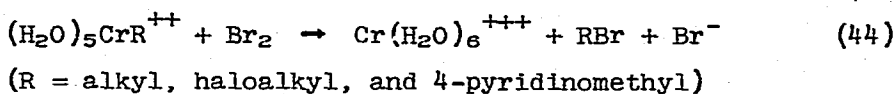
Jacobson and Wojcicki have investigated the rate of scission of the  $M-CR_3$  bond in neat  $SO_2$  at  $-65$  to  $-18^\circ$  in a group of related complexes including  $CpCr(NO)_2R$  ( $R = CH_2C_6H_5$  and  $C_6H_5$ ) and  $CpMo(CO)_3R$  ( $R = CH_3, C_2H_5, \text{ and } CH_2C_6H_5$ ).<sup>231</sup> The results obtained support the general mechanism proposed previously by these workers which involves the intermediacy of O-

bonded sulfinates in  $\text{SO}_2$  insertion reactions in alkylmetal derivatives (eq 43). Trends in rate data for a variety of



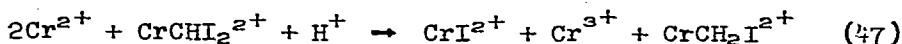
metalalkyl- $\text{SO}_2$  insertion reactions were given as well as comparison of these data with similar data for CO insertion processes.

Metal-carbon bond cleavage by halogens was kinetically studied for the systems illustrated by eqs 44<sup>232</sup> and 45.<sup>233</sup> A second order rate expression (eq 46) was dependent on R in both studies; for example  $k_2$  was related to the Hammett substituent constants of the para-substituted benzyl derivatives and this was taken as supportive evidence of an  $\text{S}_{\text{E}}2$  mechanism.



$$\text{rate} = k_2[\text{CrR}^{2+}][\text{X}_2] \quad (46)$$

Iodomethylpentaquochromium(III) is reduced by the chromous ion yielding methane.<sup>234</sup> Kinetic and activation energy parameters led the authors to suggest a long-lived organochromium intermediate of the known form  $[\text{CrCH}_3]^{+2}$  and an unknown  $[\text{CrCH}_2\cdot]^{+2}$  species as being important in the reaction sequence. In a related study the quantitative reduction of  $\text{CrCHI}_2^{2+}$  by  $\text{Cr}^{2+}$  according to eq 47 was found to be first order in each Cr reagent

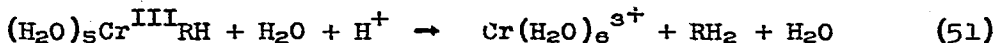
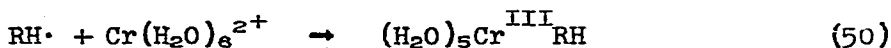
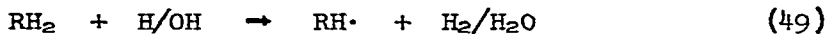


and is rate-determined presumably by a bridged transition state,  $[\text{Cr}-\text{CHI}-\text{ICr}]^{4+}$ .<sup>235</sup> Addition of labelled  $^{51}\text{Cr}^{2+}$  led to a distribution of label in all products, suggestive of a second dinuclear intermediate,  $[\text{Cr}-(\text{CHI})-\text{Cr}]^{4+}$ , carbon bridged.

Kinetic data were collected on the exchange reaction (eq 48) ( $*\text{Cr}^{++} = ^{51}\text{Cr}^{2+}$ ) and were at variance with those of earlier workers.<sup>236</sup> The present data were interpreted in terms of an  $\text{S}_{\text{H}}2$  process at the saturated carbon center, or as an inner sphere redox process involving a rather unorthodox bridging ligand.



An impressive study of the reaction of 16 aliphatic radicals, as produced by pulse radiolysis (eq 49), with  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  was reported by Cohen and Meyerstein.<sup>237</sup> Specific rates of the Cr-RH formation (eq 50) are very high, approaching diffusion



controlled, and showed no pH dependence. The order of reactivity of radicals, e.g.,  $\cdot\text{CH}_2\text{OH} > \cdot\text{CH}(\text{CH}_3)\text{OH} > \cdot\text{C}(\text{CH}_3)_2\text{OH}$ , indicated electron releasing groups enhance the probability of the unpaired electron being on the reacting carbon. Suggestions for the mechanism of certain radical rearrangements in the decomposition process (eq 51) were offered. Hexaaquochromium(II) was found to react with H atoms produced by the pulse radiolysis of water to form the  $[\text{Cr}(\text{H}_2\text{O})_5\text{H}]^{++}$  complex whose absorption spectrum is similar to analogous complexes containing a Cr-C bond.<sup>238</sup> The formation of the hydrido complex and its decomposition were followed kinetically; a seven-coordinate intermediate was suggested in the formation process.

Several kinetic and mechanistic studies dealt with  $\pi$ -arene metal carbonyl complexes. The rate constant ratios ( $k_D/k_T$ ) for proton exchange between (benzene) $\text{Cr}(\text{CO})_2\text{PPh}_3$  (labelled in the benzene ring with D or T) and  $\text{CF}_3\text{CO}_2\text{H}$  were determined and no isotopic effect was noted.<sup>239</sup> However electron-acceptor substituents on the arene ligand such as  $\text{MeCO}$ ,  $\text{MeO}_2\text{C}$ , and  $\text{Me}_2\text{N}$  were found to influence the rate of hydrogen isotope exchange of such complexes as  $\text{RPhCr}(\text{CO})_2(\text{PPh}_3)$ .<sup>240</sup> The acetyl and protonated  $\text{Me}_2\text{N}$  groups accelerated the reaction. However the  $\text{Me}_2\text{N}$  group underwent protodeamination. Further studies of the kinetics of H-D exchange on  $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  have also been reported.<sup>241</sup>

Gubin and co-workers have investigated the kinetics of  $\text{S}_{\text{N}}1$  solvolysis of  $\pi$ -(tricarbonylchromium)cumyl chloride and  $p$ - $[\pi$ -(tricarbonylchromium)phenyl]cumyl chloride in 90% aqueous acetone.<sup>242</sup> Rates of solvolysis were found to be significantly faster in these tricarbonylchromium derivatives when compared with those of the uncoordinated cumyl chlorides. The experi-

mental data were used to determine  $\sigma_p$  and  $\sigma_p^+$  constants for the  $(CO)_3CrC_6H_5$ -substituent and those values were +0.15 and -0.09, respectively. These are to be compared with the values -0.01 and -0.179 for the  $C_6H_5$ -substituent.

The displacement of the ring ligand in  $(\underline{h}^6-C_7H_8)M(CO)_3$  ( $M = Cr, Mo, W$ ) or  $(\underline{h}^6-C_6H_3Me_3)Mo(CO)_3$  with three  $CH_3CN$  has been kinetically investigated.<sup>243</sup> The observed third order rate expression for the former reaction,  $rate = k[complex][CH_3CN]^2$ , was interpreted in terms of a fast pre-equilibrium association of the arenetricarbonyl with one  $CH_3CN$  and a subsequent rate-determining reaction with a second  $CH_3CN$ .

Decomposition reaction rates for  $(arene)Cr(CO)_2L$  ( $L = CO$  or  $PPh_3$ ) have been determined. The triphenylphosphine derivative decomposed at a faster rate than the tricarbonyl analog.<sup>244</sup> The kinetic parameters for the thermal decomposition of  $W(CO)_6$  and  $Mo(CO)_6$  have also been reported.<sup>245,246</sup>

Studies of the kinetics and mechanism of reduction of  $Cr(NH_3)_5NO^{++}$  by  $Cr^{++}$  have led Armor, *et al.*, to propose coordinated hydroxylamine as an important intermediate in this reaction.<sup>247</sup>

Ceccon and Catelani have continued their investigations of the rates of side chain reactions in arenechromium tricarbonyl derivatives.<sup>248,249</sup> A study involving solvent and deuterium isotope effects in  $E_2$  reactions of some 2-phenylethyl and 1-phenyl-2-propyl derivatives was carried out. In addition, Ceccon has studied elimination reactions from (1-phenyl-1-chloropropane)-, (1-phenyl-2-propyl bromide)- and (1-phenyl-2-propyl tosylate)-chromium tricarbonyl induced by halide ions in acetone.<sup>249</sup>

Kinetic measurements on the hydroxylation of naphthalene to

$\alpha$ -naphthol by molecular oxygen in the presence of  $\text{Mo}(\text{CO})_6$  have been carried out.<sup>250</sup>

### Catalysis

The catalysis section will be presented in the following order: VIb-containing catalysts on solid supports, olefin metathesis reactions, polymerizations, hydrogenations, photochemical processes, and miscellaneous studies.

Several studies further delineate the conditions for heterogeneous catalysts composed of Cr, Mo, and W on supports such as silica or alumina. Molybdenum and tungsten hexacarbonyl, deposited on alumina, reduced with hydrogen and reacted with phosphine at 200°C, produce phosphides containing on the average 9% Mo, 6% P and 7% W, 8% P.<sup>251</sup> Along with other transition metal phosphides, the surface properties of these compounds were probed as to a variety of catalytic reactions such as  $\text{H}_2$ -1-butene,  $\text{H}_2$ -acetylene, and  $\text{H}_2$ -ethylene.

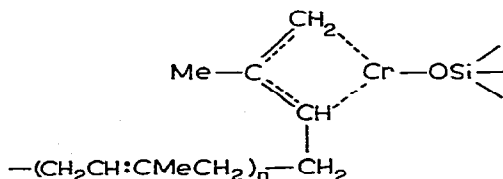
Smith, Howe and Whan have studied the disproportionation reaction of propene employing the supported  $\text{Mo}(\text{CO})_6$  catalyst on  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$ , and  $\text{MgO}$ .<sup>252</sup> The disproportionation reaction was found to be dependent on the temperature at which the support was outgassed before the addition of  $\text{Mo}(\text{CO})_6$  as well as on the temperature of activation after the addition. The disproportionation and isomerization reactions of 1-butene, cis-2- and trans-2-butene over the supported molybdenum catalyst (5%  $\text{Mo}(\text{CO})_6$ - $\gamma$ -alumina) have also been examined.<sup>253</sup>

The importance of the precursor for the preparation of heterogeneous catalysts systems has been demonstrated in two works. Hexamethyltungsten, thermally less stable than  $\text{W}(\text{CO})_6$ ,



was supported on silica or alumina, and, when activated at 373°K, produced a catalyst system with activity towards room temperature propene disproportionation comparable to those derived from  $\text{Mo}(\text{CO})_6$ .<sup>254</sup> Thus the three precursors were compared as to catalytic activity:  $\text{Mo}(\text{CO})_6 > \text{WMe}_6 > \text{W}(\text{CO})_6$ . Comparison of a more extensive series of Mo and W compounds impregnated on  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  showed highest propene disproportionation catalytic activity for the organometallic derivatives such as  $\text{M}(\text{CO})_6$  or  $\text{MR}_6$  ( $\text{R} = \text{Me}, \text{CH}_2\text{CMe}_3, \text{CH}_2\text{SiMe}_3$ ) and of those, the highest activity was obtained from the less thermally stable precursors.<sup>255</sup> High oxidation state derivatives were also investigated and found to be suitable catalysts providing they be readily reduced at some stage during catalyst preparation.

The polymerization of butadiene or isoprene on tris( $\pi$ -allyl)-chromium-silica gel or -aluminosilicate supported catalysts were found to give diene rubber with 92-7% 1,4-trans units.<sup>256</sup> On the other hand tris( $\pi$ -allyl)chromium supported on  $\text{Al}_2\text{O}_3$  afforded a polydiene containing 83-95% 1,4-cis units. The stereospecificity of tris( $\pi$ -allyl)chromium-silica gel and -aluminosilicate catalytic systems was suggestive of reactive centers having structure (LIX).



(LIX)

Several other studies utilizing  $\pi$ -allyl-VIb supported catalysts were reported.<sup>257</sup> The activity of tetrakis- $\pi$ -allyl-

molybdenum supported on silica gel towards the preparation of  $\text{NH}_3$ <sup>258</sup> and also towards the oxidation of  $\text{H}_2$ <sup>259</sup> has been examined.

Supported molybdena catalysts have been employed in the formation of maleic anhydride from the vapor phase oxidation of butadiene.<sup>260</sup>

Intermediates of interest as to the role of metal-carbene complexes in cyclopropanation and olefin metathesis reactions were proposed by Casey and Burkhardt in a study which involved the diphenylcarbene complex,  $\text{W}(\text{CO})_5\text{C}(\text{Ph})\text{Ph}$ .<sup>261</sup>

Several olefin metathesis studies involved VIB compounds in the presence of aluminum halides as the catalyst system. Markó and co-workers have found that  $\text{W}(\text{CH}_2\text{C}_6\text{H}_5)_4$  in the presence of  $\text{AlCl}_3$  catalyzes the disproportionation and cis-trans isomerization of linear olefins. Using this catalyst 2-pentene disproportionates to 2-butene and 3-hexene.<sup>262</sup> On the other hand if  $\text{W}(\text{CH}_2\text{C}_6\text{H}_5)_4$  was combined with  $\text{C}_2\text{H}_5\text{AlCl}_2$  as a cocatalyst, the initial catalytic activity disappeared completely within a few minutes. In another work it was shown that highly reactive Lewis salt adducts of halocarbonyl and halonitrosyl complexes of molybdenum and tungsten with  $\text{AlCl}_3$  and  $\text{AlEtCl}_2$  are present in homogeneous olefin disproportionation catalyst mixtures.<sup>263</sup> The metathesis of cis-2-pentene over  $\text{Ph}_3\text{PW}(\text{CO})_5$  in the presence of  $\text{EtAlCl}_2$  and oxygen was found to give mixtures of cis- and trans-2-butene with an increasing proportion of trans-2-butene as the percent conversion increased.<sup>264</sup> Further studies involving the effects of oxygen on the metathesis reaction of cis-2-pentene using  $\text{Ph}_3\text{PW}(\text{CO})_5$  and  $\text{EtAlCl}_2$  as cocatalysts have been reported.<sup>265</sup>

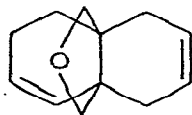
Co-condensation of Cr atoms in the presence of  $[\text{Et}_2\text{AlCl}]_2$

produced a catalyst system efficient towards the oligomerization of butadiene to cyclododecatriene.<sup>266</sup> Several other metal systems were compared.

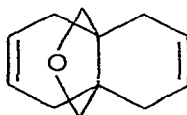
Polymerization of acetylenes has been accomplished using (arene)M(CO)<sub>3</sub> (M = Mo, Cr) species as catalysts.<sup>267</sup> For example, poly(phenylacetylene) was prepared rapidly and quantitatively in the presence of (toluene)molybdenum tricarbonyl to give a high molecular weight polymer (12,000). Polymerization reactions of methylmethacrylate at 40-60° initiated by Mo(CO)<sub>6</sub> and CCl<sub>4</sub> have been examined by Bamford and Sakamoto.<sup>268</sup> Included in this study was the determination of absolute rate coefficients for redox reactions of CCl<sub>4</sub>, CCl<sub>3</sub>CO<sub>2</sub>Et and CBr<sub>4</sub> with the complex formed by photolysis of Mo(CO)<sub>6</sub> in methylmethacrylate.

Tetra- $\pi$ -allylmolybdenum or tetra- $\pi$ -crotylmolybdenum when reacted with trichloroacetic acid, trifluoroacetic acid, hydrochloric acid or bromine were shown to give R<sub>3</sub>MoX-type complexes which were stereospecific catalysts in the polymerization of butadiene to polybutadiene elastomer with predominantly the 1,2-structure.<sup>269</sup>

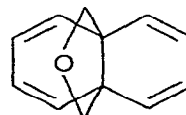
Hydrogenation of 12-oxo[4.4.3]propella-2,4,7,9-tetraene (LX) catalyzed by (phenanthrene)chromiumtricarbonyl has afforded the diene species (LXI and LXII).<sup>270</sup> Homogeneous hydrogenation



(LX)



(LXI)



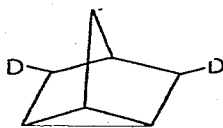
(LXII)

of 1,3- or 1,4-dienes to monoenes using dicyclopentadienyldihydromolybdenum as a catalyst under 160 atm of hydrogen has

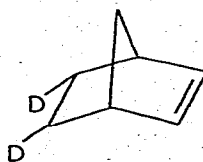
been investigated.<sup>271</sup> Tris(acetonitrile)tricarbonylchromium has also been shown to catalyze 1,4-addition of hydrogen to 1,3-dienes (e.g., 2-methyl-1,3-butadiene, trans-1,3-pentadiene, and trans,trans-2,4-hexadiene) under very mild thermal conditions.<sup>272</sup>

The Pd/C-catalyzed deuteration of syn-(dibenzobicyclo[2.2.2]octatriene)tricarbonylchromium has led to the production of syn-(dibenzobicyclo[2.2.2]octadiene)tricarbonylchromium as a predominantly  $d_2$  species with both D on the ethano bridge and anti to the  $Cr(CO)_3$  moiety.<sup>273</sup>

Platbrood and Wilputte-Steinert have investigated the mechanism of the photoinduced hydrogenation of norbornadiene catalyzed by (norbornadiene) $Cr(CO)_4$ .<sup>274</sup> A mechanism was proposed which involved initial metal-olefin bond rupture with no metal-CO bond cleavage. In addition, these workers have studied the mechanism of the photoinduced hydrogenation of 2,4-hexadiene catalyzed by  $Cr(CO)_3$  or (norbornadiene) $Cr(CO)_4$ .<sup>275</sup> The selectivity of the reaction with respect to the three isomers of 2,4-hexadiene depends on the nature of the precatalyst employed. In another study, irradiation of 1,3-cyclohexadiene under one atmosphere of  $D_2$  in pentane with  $Cr(CO)_3$  or (norbornadiene) $Cr(CO)_4$  as catalyst was shown to yield exclusively cyclohexene-3,6- $d_2$ .<sup>276</sup> Similarly treatment of 2,4-hexadiene gave 96% cis-3-hexene-2,5- $d_2$  and norbornadiene gave 65% nortricyclene-3,5- $d_2$  (LXIII) and 35% endo,endo-norbornene-5,6- $d_2$  (LXIV).



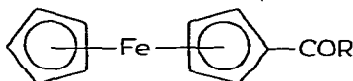
(LXIII)



(LXIV)

Wrighton, Hammond and Gray have studied Group VIb metal carbonyl photoassisted rearrangement reactions of olefins, including both cis-trans isomerization and 1,3-hydrogen shifts.<sup>277</sup> Ultraviolet irradiation of  $M(CO)_6$  ( $M = Cr, Mo, \text{ or } W$ ) in the presence of olefin was observed to yield light-sensitive metal carbonyl-olefin complexes which underwent further photosubstitution of CO and olefin with high quantum efficiency. A general mechanistic scheme for these reactions was discussed. A variety of allylsilanes have been prepared by the  $Cr(CO)_6$  photocatalyzed 1,4-hydrosilation of 1,3-dienes.<sup>278</sup>

The following catalyst systems are grouped together in a miscellaneous category. The selective gas-phase oxidation of butene and butadiene to maleic anhydride and HCHO on a Fe-Mo catalyst has been examined.<sup>279</sup>  $Mo(CO)_6$  has been used as a catalyst in the preparation of acylated ferrocenes (LXV) from ferrocene and  $RCOCl$ .<sup>280</sup> Further studies on organometallic



(LXV)

R = Me, Me<sub>2</sub>CH, cyclohexyl, 1-adamantyl, Ph

polymers involving Group VIb metals have been carried out by Pittman and Marlin. The synthesis and copolymerization behavior of the ( $\pi$ -phenylethyl acrylate)chromium tricarbonyl derivative was examined.<sup>281</sup>

$\alpha$ -Diazo carbonyl compounds in the presence of nitriles and  $WCl_6$  have afforded oxazoles in 20-66% yields, e.g.,  $PhCOC(:N_2)Ph$  with  $CH_2=CHCN$  and  $WCl_6$  gave 50% 2-vinyl-4,5-diphenyl-

oxazole. The tungsten catalytic activity was attributed to the affinity of tungsten for carbenes.<sup>282</sup>

### Spectroscopic Studies

Electronic spectra and related photolysis studies. U.V. and visible absorption spectra of a number of  $M(CO)_5X$  compounds, including the monoanions of  $M = Mo, Cr, W$ ;  $X = Cl, Br, I$ , have been measured and interpreted using a new M.O. bonding scheme and correlated with pes results.<sup>283</sup> The LUMO was ascertained to be mainly a  $\sigma^*$  orbital of the M-X bond rather than a  $\pi^*(CO)$ . The reader is further referred to reference 355.

Infrared and Raman spectra. The inability of annealing at 40-45°K to change the ir spectral bands attributed by other workers to  $C_{4v} Cr(CO)_5$  led Ozin and Kündig to propose that the vacant site of  $Cr(CO)_5$  as formed from co-condensation of Cr and pure CO was actually blocked by an O-bonded isocarbonyl or a sideways-bonded CO group.<sup>284</sup> In Ar matrices,  $D_{3h} Cr(CO)_5$  is believed to form.

The synthesis of a series of monosubstituted derivatives of chromium,  $LCr(CO)_5$ , where  $L = (C_6H_5)_3E$  and  $(4- \text{ or } 3-XC_6H_4)_3E$  ( $E = P, As, Sb$  and  $X = Cl, F$ ) has been reported.<sup>285</sup> The  $\nu(CO)$ , including two  $^{13}CO$  vibrations,  $\nu(M-C)$  and  $\delta(M-C-O)$  vibrations were assigned and discussed. Bis(ditolylarsino)methane ligands have been synthesized and their derivatives with  $Mo(CO)_6$  have been prepared.<sup>286</sup> Nmr and ir spectroscopy was used to study steric effects within these substituted metal carbonyl complexes.

The infrared and Raman spectra of norbornadiene and the Group VIb tetracarbonyl(norbornadiene)metal(O) complexes have

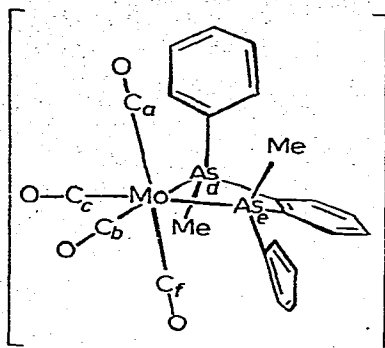
been measured by Butler and Barna.<sup>287</sup> The metal-olefin stretching modes were observed at 210-250  $\text{cm}^{-1}$ . A similar study on the chromium and molybdenum norbornadiene derivatives has been carried out as well by Russian workers.<sup>288</sup>

Polarized Raman spectra in methylene chloride solution have been reported for a number of complexes of the type  $\text{LM}(\text{CO})_5$  (L = Lewis base; M = Cr, W) in the region 580-100  $\text{cm}^{-1}$ .<sup>289</sup> Assignment of the metal-carbon and ligand-metal stretching vibrations have been made using these data as well as infrared data. A linear relationship for  $\nu_{\text{CO}}(A_1^1)$  vs  $\nu_{\text{MC}}(A_1^1)$  was observed for several  $\text{LW}(\text{CO})_5$  derivatives with  $\nu_{\text{CO}}$  increasing as  $\nu_{\text{MC}}$  decreased.

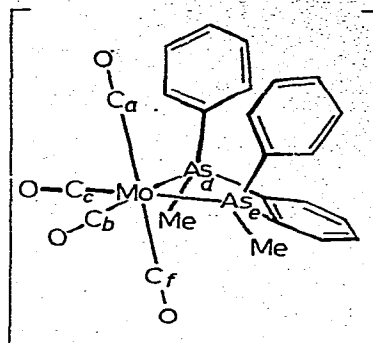
The complete Raman and ir spectra of  $[\text{CpMo}(\text{CO})_3]_2$  and  $\text{CpMn}(\text{CO})_3$  and their perdeuterated derivatives have been measured and assigned.<sup>290</sup> Comparison of solution and solid state spectra suggested that in the solid a symmetry persists which is lower than the usually assumed  $\text{C}_{5v}$  for the  $\text{C}_5\text{H}_5\text{-M}$  local symmetry. Similarly, new Raman polarization data have permitted complete assignments of the  $\pi$ -arene in several  $(\pi\text{-arene})\text{Cr}(\text{CO})_3$  complexes and also point out the failure of the "local" symmetry concept.<sup>291</sup> In another Raman spectral study, the high resolution single crystal spectra of the  $[\text{Cr}(\text{CO})_3]$  moiety of  $(\text{h}^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  and  $(\text{h}^6\text{-1,3-Me}_2\text{C}_6\text{H}_4)\text{Cr}(\text{CO})_3$  were analyzed in detail by Kettle, Buttery, and Paul.<sup>292</sup>

Nuclear magnetic resonance and Mössbauer spectra. The most extensive use of nmr spectroscopy was in the area of conformational analysis of ligands and in studies of fluxional processes. The  $^{13}\text{C}$  nmr spectra in the CO region were used to unambiguously identify the diastereoisomers of a bidentate ditertiary arsine

ligand, *o*-phenylenebis(methylphenylarsine) (L) as its derivative of molybdenum tetracarbonyl (LXVI A and B).<sup>293</sup> Further studies



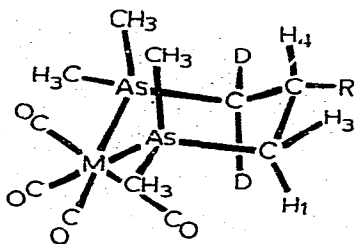
(LXVI A)



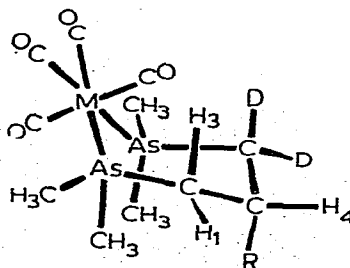
(LXVI B)

of the compounds included the  $\text{PPh}_3$  substitution reaction to yield *fac*- $\text{Mo}(\text{CO})_3(\text{PPh}_3)\text{L}$ , and the fluxional behavior of the iodine oxidation product,  $\text{Mo}(\text{CO})_3(\text{I})_2\text{L}$ .

Complete analysis of the nmr spectra of the complexes  $(\text{CO})_4\text{MAs}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{R})\text{CH}_2\text{As}(\text{CH}_3)_2$  required preparation of deuterated analogs.<sup>294</sup> The effect of the R group on the flexibility of the six-membered chelate ring was as follows: with  $\text{R} = \text{H}$ , fast conformational inversion between symmetric chair forms was observed; with  $\text{R} = \text{C}(\text{CH}_3)_3$ , the conformation was locked into form (LXVII A). In addition, proton and fluorine



(LXVII A)

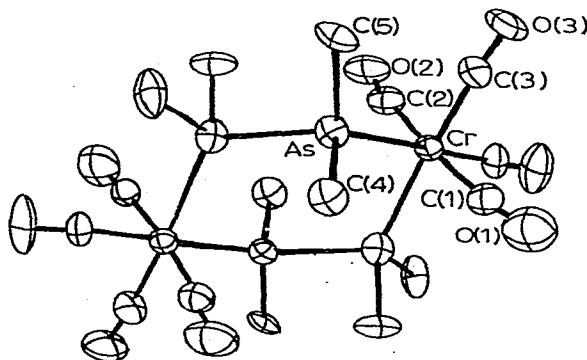


(LXVII B)



nmr studies on chelate complexes of the VIb carbonyls used similar ligands specifically designed for complete spectral analysis and rotamer conformational analysis, for example,  $\text{Me}_2\text{AsCHFCHFAsMe}_2$ ,  $\text{Me}_2\text{PCHFCHF}_2\text{PMe}_2$ , etc.<sup>295</sup> Other new metal tetracarbonyl derivatives include  $\text{LM}(\text{CO})_4$  where L is the cyclohexane analog, 1,4-diselenane,  $[\text{SeCH}_2\text{CH}_2]_2$ , and  $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ .<sup>296</sup> In these complexes L was suggested to be in a boat conformation with  $\text{M}(\text{CO})_4$  acting similarly to the  $\text{CH}_2$  bridgehead in norbornane. The  $^1\text{H}$  nmr spectra were completely analyzed.

Cotton and Webb have reported the preparation and X-ray structure of a novel metallocycle, cyclohex-1,4-(tetracarbonylchromium)-2,3,5,6-(dimethylarsenic), from the reaction of  $\text{Me}_2\text{As}(\text{O})\text{OH}$  and  $\text{Cr}(\text{CO})_6$ .<sup>297</sup> The structure of the complex consists of a six-membered ring having a chair conformation made up of two  $\text{Cr}(\text{CO})_4$  groups in the 1 and 4 positions with  $(\text{CH}_3)_2\text{As}$  groups in the remaining positions (LXVIII). Temperature-dependent



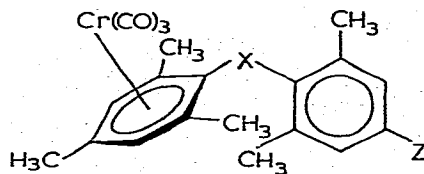
(LXVIII)

$^1\text{H}$  nmr studies yielded an estimated 10 kcal/mole as the activation energy for the interconverting of the two chair conformations (interchange of  $\text{C}(4)$  and  $\text{C}(5)$ ).

Proton nmr studies of the fluxionality of the 5-membered chelate ring system in (1,2-bisisopropylselenoethane) $M(\text{CO})_4$ ,  $M = \text{Cr}, \text{Mo}$ , were interpreted in terms of total inversion of the chelate ring.<sup>298</sup> For  $M = \text{W}$ , the nmr spectrum was temperature invariant with one ligand conformer locked in position even at 330°K, that is, covering the range in which coalescence and time averaging of signals was observed for the Cr and Mo analogs.

The four separate sharp  $^{13}\text{C}$  nmr signals of the ring carbons of ( $\text{h}^5\text{-C}_8\text{H}_8$ ) $\text{Mo}(\text{CO})_3$  broaden and collapse simultaneously as the temperature is raised above 0°C.<sup>299</sup> Cotton and co-workers ascertain that the most likely description of the fluxional character of this molecule involves a symmetrical "piano-stool" intermediate, with Mo atop the center of a flat cyclooctatetraene (COT) octagon, rather than the 1,2 shift which predominates for the 1,3,5,7-tetramethylenecyclooctatetraene (TMCOT) analog. The latter behavior, previously established by  $^1\text{H}$  nmr, was verified by  $^{13}\text{C}$  resonance studies.<sup>300</sup> The different mode of ring carbon equilibration of (TMCOT) $M(\text{CO})_3$  and (COT) $M(\text{CO})_3$  is believed to arise from different energies required to flatten the rings.

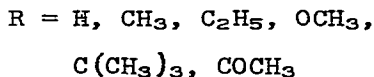
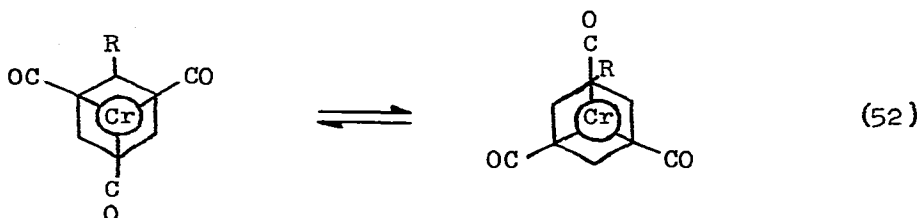
Barriers to rotation were also established by proton nmr for uncomplexed ring-carbon rotation of mono(tricarbonyl)chromium complexes of diarylmethanes and related compounds (LXIX).<sup>301</sup>



(LXIX)

That is, for  $X = \text{CH}_2$ , the ortho positions of the non-complexed mesityl group are equilibrated with a barrier of 14.3 kcal/mole at 18°C for  $X = \text{CH}_2$  whereas for  $X = >\text{C}=\text{O}$ , the barrier is substantially higher, 19.6 kcal/mole at 118°. For  $X = >\text{C}=\text{CH}_2$ , the barrier is essentially the same as for  $X = \text{CH}_2$ , suggesting very little  $\pi$ -electron interaction with the uncomplexed ring and hence stabilization of the ground state conformation as is the case with the ketone bridge.

A low temperature  $^{13}\text{C}$  nmr study of the rotation around the chromium-arene bond in a series of arenechromium tricarbonyl derivatives has been carried out (eq 52).<sup>302</sup> It was shown that complexation did not significantly change the transmission of electronic substituent effects to the para position. The thermodynamic parameters ( $\Delta H$  and  $\Delta S$ ) for this equilibrium process ranged from -0.85 to +0.40 kcal/mole and -2.53 to +4.00 e.v., respectively.

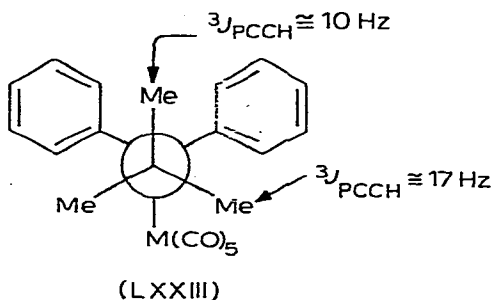


The temperature dependent  $^1\text{H}$  nmr spectra of cyclopentadienylchromium carbonyl nitrosyl ethylene,  $\text{CpCr}(\text{CO})(\text{NO})(\text{CH}_2=\text{CH}_2)$ , and its deuterated analog,  $\text{CpCr}(\text{CO})(\text{NO})(\text{CHD}=\text{CHD})$ , indicate that hindered rotation about the metal-olefin bond axis occurs (LXX).<sup>303</sup> The free energy of activation for the ligand motion was found to be  $11.4 \pm 0.2$  kcal/mole in both cases.

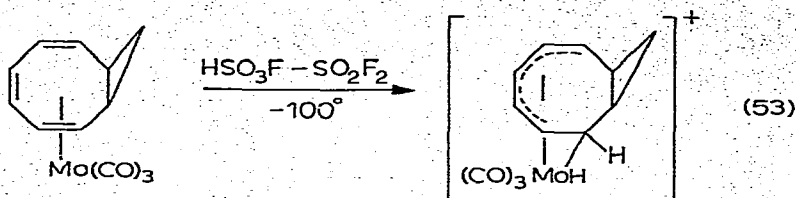


A substantially lower barrier to interconversion between anti and gauche rotamers of  $[\text{CpCr}(\text{CO})_3]_2$  as compared to the Mo analog was established by proton nmr.<sup>306</sup> At  $-10^\circ\text{C}$ , a line broadening is observed whose temperature dependent reversibility was suggestive of dissociation of the dimer into stable radicals of  $\text{CpCr}(\text{CO})_3$ . Further studies of barriers to internal rotation were extended to the isostructural  $\text{Cp}_2\text{W}_2(\text{CO})_6$ .<sup>307</sup> X-ray structure metal-metal bond distances of 3.281, 3.235 and 3.222 Å for Cr-Cr, Mo-Mo, and W-W, respectively, were correlated with increasing barriers to equilibration; the corresponding  $\Delta G^\ddagger$  values were found to be 12.1, 15.2 and 16.2 kcal/mole, respectively. The more rapid rotation of the Cr compound was attributed to a repulsion dominated internal barrier to Cr-Cr rotation, giving rise to both more favorable  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  parameters.

Activation energy parameters ( $\Delta H^\ddagger \cong 9 \text{ kcal mol}^{-1}$ ;  $\Delta S^\ddagger \cong 2 \text{ gibbs}$ ) for *t*-butyl rotation about the C-P single bond in  $(\text{t-Bu})\text{Ph}_2\text{PM}(\text{CO})_5$  ( $\text{M} = \text{Cr, Mo, W}$ ) were completely insensitive to M.<sup>308</sup> This study however showed P-H coupling constants to be a useful probe of the complexed phosphine stereochemistry as illustrated in LXXIII.



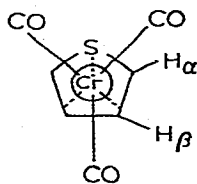
Brookhart and Harris suggested that their previously established  $\pi$  to  $\sigma$  rearrangements re eq 53 might explain other results



in the literature, notably proton scrambling of protonated diene iron carbonyl species.<sup>309</sup>

Many studies reported dealt with the electronic nature of VIb complexes as probed by nmr spectroscopy. Fluorine-19 nmr was used as a probe of the degree of metal-diazonium ligand  $\pi$ -bonding in complexes such as  $\text{CpMo}(\text{CO})\text{PPh}_3(\text{N}_2\text{-Ar})$  ( $\text{Ar} = m\text{-FC}_6\text{H}_4, p\text{-FC}_6\text{H}_4$ ) and some 14 others.<sup>310</sup> Specifically, the difference in chemical shift values,  $^{19}\text{F}(\delta_{\underline{p}} - \delta_{\underline{m}})$ , were in agreement with the order of  $\text{M} \rightarrow \text{N}_2\text{-Ar}$   $\pi$ -bonding anticipated on basis of relative donor and acceptor power of the co-ligands and on the oxidation state of the metal. The  $\nu(\text{NN})$  stretching frequencies were analyzed by the aid of  $^{15}\text{N}^{14}\text{N}$  labelling.

Several (thiophene) $\text{Cr}(\text{CO})_3$  complexes have been investigated by  $^1\text{H}$  nmr spectroscopy.<sup>311</sup> The shielding of the  $\alpha$  relative to the  $\beta$  protons (LXXIV) was interpreted in terms of increased charge density on the  $\alpha$  carbon atoms.



(LXXIV)

Anderson has studied a variety of solid metallocene, dibenzene, and dicyclooctatetraenyl metal complexes via wide-

line nmr spectral measurements in the temperature range 178-381°K.<sup>312</sup> Included in this study were the chromium derivatives;  $\text{Cr}[\text{C}_6(\text{CH}_3)_6]_2\text{I}$ ,  $\text{Cr}(\text{C}_6\text{H}_6)_2$ , and  $\text{CrCp}_2$ .

Fourier-transform  $^{13}\text{C}$  nmr data, measured on  $(\text{h}^6\text{-C}_6\text{H}_5\text{X})\text{Cr}(\text{CO})_3$  ( $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Me}, \text{OMe}, \text{NH}_2$ , etc.), were interpreted to mean a net withdrawal of electron density by the chromium carbonyl moiety from the  $\sigma$  framework of the arene ring.<sup>313</sup> Furthermore these studies by Bodner and Todd indicated a shielding effect on carbonyl carbon chemical shifts with increasing donor ability of the  $\pi$ -arene substituent.<sup>314</sup> Additional data on an  $\text{LM}(\text{CO})_5$  series supported the author's contention that the CO chemical shifts are a linear measure of the extent of transition metal  $\rightarrow$  carbonyl  $\pi$ -back-donation. Other workers have pointed out contradictory explanations of  $^{13}\text{C}$  chemical shifts of carbon atoms both  $\sigma$  and  $\pi$ -bound to transition metals.<sup>315</sup> For example, the linear relation of transition metal  $\rightarrow \pi$ -back-donation with  $^{13}\text{C}$  chemical shift in CO compounds holds only for very closely related compounds.

The isotropic shifts of the  $^{11}\text{B}$  and  $^{13}\text{C}$  nuclear resonances in paramagnetic metallocarboranes such as  $[\text{M}(2,3\text{-C}_2\text{B}_9\text{H}_9(\text{Me}_2)_2)]^-$  ( $\text{M} = \text{Cr}^{\text{III}}, \text{Fe}^{\text{III}}$ ) were determined to reflect large negative nuclear-electron hyperfine coupling constants, consistent with parallel spin transfer from ligand to metal.<sup>316</sup>

$^{13}\text{C}$  and  $^1\text{H}$  nmr studies of the compounds  $\text{CpM}(\text{C}_7\text{H}_7)$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Mo}, \text{Cr}$ ) have been carried out by Groenenboom and Jellinek.<sup>317</sup> In the chromium compound the  $^{13}\text{C}$  resonance of the  $\text{C}_7\text{H}_7$  ring was observed at lower field than that of the Cp ring, while for the molybdenum compound the two signals lie close together.  $^1\text{H}$  nmr spectra indicate hindered rotation of the rings in the Cr and

Mo compounds. The  $^{13}\text{C}$  nmr spectrum of indenochromium tricarbonyl,  $(\text{C}_9\text{H}_8)\text{Cr}(\text{CO})_3$ , was included in comparisons of indene and several of its complexes.<sup>318</sup>

The synthesis of  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{OPPh}_2$  ( $n = 1, 2$ ) and properties of the  $(\text{L}-\text{L}')\text{M}(\text{CO})_4$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) derivatives have been reported.<sup>319</sup> Nmr studies showed P-P coupling to be enhanced upon coordination due to the "through metal" contribution, and also showed interesting, unexplained  $^{31}\text{P}$  chemical shifts that were dependent on chelate ring size. A convenient review of the effect of coordination on  $J_{\text{P}-\text{P}}$  and  $J_{\text{P}-\text{H}}$  was given in this paper. Continuing the unsymmetrical phosphorus ligand work, Grim and co-workers described the preparation and properties of VIb metal carbonyl complexes of  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhR}$  ( $\text{R} = \text{Me}, \text{Et}, \text{i-Pr}$ , etc.) and  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{n-Bu})_2$ .<sup>320</sup> Reaction of  $\text{M}(\text{CO})_6$  with the ligands in hot diglyme gave  $(\text{P}\sim\text{P}')\text{M}(\text{CO})_4$  or  $(\text{CO})_5\text{MoP}\sim\text{P}'\text{Mo}(\text{CO})_5$ . A mononuclear, monodentate complex exhibiting linkage isomerism as verified by  $^{31}\text{P}$  nmr was prepared by the labile ligand technique using  $\text{PhNH}_2\text{W}(\text{CO})_5$  and  $\text{i-PrPhPCH}_2\text{CH}_2\text{PPh}_2$ .

The  $^{31}\text{P}$  nmr spectra of  $\text{W}(\text{CO})_3(\text{TP})$  and  $\text{W}(\text{CO})_3(\text{QP})$  ( $\text{TP} = (\text{o-Ph}_2\text{PC}_6\text{H}_4)_2\text{PPh}$  and  $\text{QP} = (\text{o-Ph}_2\text{PC}_6\text{H}_4)_3\text{P}$ ) have been measured employing both continuous wave and FT techniques.<sup>321</sup> Both molecules were shown to exist as the facial isomers based on the  $^{183}\text{W}-^{31}\text{P}$  coupling constant values.

The mono-ligated  $\text{W}(\text{CO})_5(\text{PPh}_2\text{CH}=\text{CHPPh}_2)$  and  $\text{W}(\text{CO})_5(\text{PPh}_2\text{C}\equiv\text{CPPh}_2)$  and their quaternized forms were prepared and compared with other L-L and L-L<sup>+</sup> monodentate ligands containing saturated linkages.<sup>322</sup> The relative values of the tungsten to free phosphorus coupling constants (or to free phosphonium) were not significantly affected by the type of linkage, saturated or unsaturated.



Only two Mössbauer studies involving VIb metal-organics were reported. The tin-119m Mössbauer shifts of the Group VIb metal derivatives of  $\text{SnCl}_3^-$ ,  $\text{M}(\text{CO})_5\text{SnCl}_3^-$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) have been observed to be 2.04, 2.12 and 1.87 mm/sec, respectively with corresponding quadrupole splitting parameters of 1.86, 1.94 and 2.00 mm/sec.<sup>323</sup> These results were taken to mean that these derivatives should be considered as Sn(IV) species with a noticeable  $\pi$ -backbonding ability of the  $\text{SnCl}_3$  ligand. Mössbauer studies of several tungsten salts, including  $\text{W}_2\text{C}$ , using the 100 keV transition of tungsten-182 were reported.<sup>324</sup>

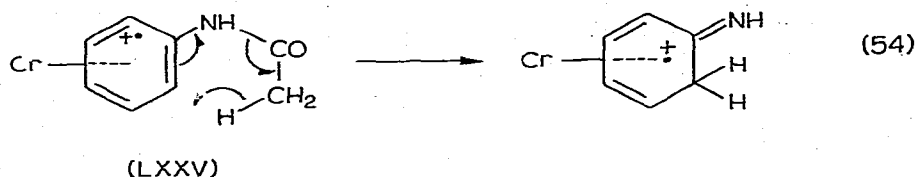
Esr spectra. Franz, et al. have reduced glyoxal- and diacetyl-bis(imine)metal tetracarbonyls  $(\text{RN}=\text{CR}'-\text{CR}'=\text{NR})\text{M}(\text{CO})_4$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) with potassium in DME to give the paramagnetic mono-anions.<sup>325</sup> The high-resolution ESR spectra of these species show the hyperfine splitting of the magnetically active atoms in the ligand as well as the satellites of the metal isotopes  $^{53}\text{Cr}$ ,  $^{95,97}\text{Mo}$  and  $^{183}\text{W}$ . The coupling constants were discussed in terms of a  $\pi$ -bonding mechanism.

The solvent and temperature dependent esr spectra of the tetravalent chromium compound, tetrakis(1-norbornyl)chromium suggest that the compound assumes several conformations in isooctane and cyclohexane glasses.<sup>326</sup> The synthesis of  $(\text{nor})_4\text{Cr}$  from 1-norbornyllithium and  $\text{CrCl}_3 \cdot 3\text{THF}$  was also described.

Electron paramagnetic resonance and infrared spectral studies of some nitrosyl derivatives of chromium have been reported.<sup>327</sup> The complexes involved in this study were of the type  $\text{CrL}_2(\text{NO})(\text{OH}_2)$ , where HL = salicylaldoxime,  $\alpha$ -nitroso- $\beta$ -naphthol, 8-hydroxyquinoline, 8-thioquinoline and disodium 1-nitroso-2-hydroxynaphthalene-3,6-disulfonate. In another

study the EPR spectra of  $[\text{Cr}(\text{CN})_5\text{NO}]^{-3}$  ions were measured in polycrystalline powders and solutions.<sup>328</sup> Further studies on the EPR spectra of nitrosyl chromium compounds have also been reported.<sup>329</sup>

Mass spectra. Mass spectral studies of acetanilidetri-carbonylchromium and its 2,4- and 2,6-dimethyl analogs indicate that ketene elimination from  $[(\text{C}_6\text{H}_5\text{NHCOCH}_3)\text{Cr}]^+$  (eq 54) occurs via a six-membered transition state (LXXV).<sup>330</sup>



An interpretation of the 50 eV mass spectra of  $\text{M}(\text{CO})_5\text{PR}_3$  complexes ( $\text{M} = \text{Cr}$  and  $\text{W}$ ,  $\text{R} = \text{OCH}_3$ ,  $\text{OC}_2\text{H}_5$ ,  $n\text{-C}_4\text{H}_9$ ,  $o\text{-}n\text{-C}_4\text{H}_9$  and  $\text{C}_6\text{H}_5$ ) by means of appearance potential measurements has been carried out by Torrioni, Innorta, Foffani, and Distefano.<sup>331</sup> Other mass spectral studies (including appearance ionization potentials) for a series of (arene)chromiumtricarbonyl derivatives have been reported (arene =  $\text{C}_6\text{H}_6$ ,  $\text{MeC}_6\text{H}_5$ ,  $\text{EtC}_6\text{H}_5$ ,  $\text{Me}_2\text{CH-C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5\text{Cl}$ ,  $\text{C}_6\text{H}_5\text{F}$  and  $\text{C}_6\text{H}_5\text{I}$ ).<sup>332</sup> Furthermore the feasibility of mass spectral analysis of mixtures of  $(\text{CO})_3\text{CrPhX}$  derivatives ( $\text{X} = \text{H}$ ,  $\text{Me}$ ,  $\text{Et}$ ,  $\text{F}$  and  $\text{Cl}$ ) has been investigated by Larin and Galvoronskii.<sup>333</sup>

Mass spectral studies of dicyclopentadienyl pi complexes of  $\text{V}$ ,  $\text{Cr}$ ,  $\text{Fe}$  and  $\text{Ni}$  have been reported,<sup>334</sup> as well as of the hexacarbonyls  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}$ ,  $\text{Mo}$ ,  $\text{W}$ ).<sup>335</sup>

The use of field mass spectroscopy for studying the kinetics

of the thermal decomposition reaction of  $(EtPh)_2Cr$  has been examined.<sup>336</sup> Additional studies of this type have been carried out on a variety of bis(arene) derivatives of chromium and molybdenum.<sup>337</sup>

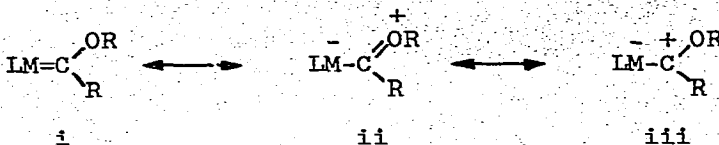
The methane chemical ionization mass spectra of  $ArCr(CO)_3$  (Ar = benzene, toluene, mesitylene, chlorobenzene, fluorobenzene and methyl benzoate), mesitylenemolybdenum tricarbonyl, cycloheptatrienechromium tricarbonyl, and dibenzenechromium were interpreted in terms of predominant metal protonation of the complexes.<sup>338</sup>

Ion-molecule reactions of the carbene complex  $(CO)_5CrC(CH_3)OCH_3$  have been reported by Müller and Goll.<sup>339</sup> In another study the electron impact induced fragmentation of a variety of heterocyclic carbene ligands bound to  $Cr(CO)_5$  has been investigated by Müller and co-workers.<sup>340</sup>

#### Photoelectron spectra and molecular orbital calculations.

In addition to the following five pes studies the reader is also referred to reference 283.

Relative core binding energies of all atoms in  $(CO)_5CrC(OCH_3)CH_3$  have been determined by X-ray photoelectron spectroscopy. The binding energies of all carbon 1s electrons in the  $-C(OCH_3)CH_3$  ligand (-2.7, -1.4, -1.4 eV, respectively) were found to be lower than carbonyl carbons (-.07), thus suggesting that carbene ligand carbons carry less positive charge.<sup>341</sup> Correlation of C, O, and Cr binding energies with calculated atomic charges necessitated using hybrids i, ii, and iii weighted 45%, 20%, and 35%, respectively.



Correlation of ESCA electron binding energies with charge on Mo promoted the efficacy of X-ray photoelectron spectroscopy as a tool for determining the mode of metal nitrosyl bonding.<sup>342</sup> In addition to the compound,  $\text{MoCl}_2(\text{NO})_2(\text{PPh}_3)_2$ , spectra were interpreted for  $\text{Mo}(\text{CO})_5\text{PPh}_3$  and  $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ . Photoelectron spectra of monosubstituted carbonyl complexes of chromium and tungsten of the type  $\text{M}(\text{CO})_5\text{L}$  (L = amine, phosphine, or isonitrile) were also measured.<sup>343</sup> The assignment of bonds was aided by SCF MO calculations on  $\text{Cr}(\text{CO})_5\text{L}$  (L =  $\text{NH}_3$  or  $\text{PH}_3$ ).

Preliminary results of ESCA measurements employing Mg-K $\alpha$  radiation (1253.6 eV) on the cyclopentadienylcycloheptatrienyl-metal complexes  $\text{CpM}(\text{C}_7\text{H}_7)$  (M = Ti, V, and Cr) revealed that the oxidation state of the metal increased in the sequence  $\text{Cr} < \text{V} < \text{Ti}$ .<sup>344</sup> In another study, the  $\pi$ -arene sandwich compounds, bis-mesitylenechromium(0) and molybdenum(0), bis-toluenemolybdenum(0), dibenzenemolybdenum(0), and (cycloheptatrienyl)(cyclopentadienyl)-chromium(0) were included in a He(I) photoelectron spectroscopy study.<sup>345</sup>

Molecular orbital calculations have been carried out on the series of metal dimers  $[\text{Cr}_2(\text{CO})_8(\mu_2\text{-PR}_2)_2]^{(n-2)}$  (n = 0, +1, and +2).<sup>346</sup> These computations indicated that the species with n = 0, +1, and +2 have two, one, and no electrons, respectively, in the antibonding  $2b_{3u}$  molecular orbital which corresponds to a "net" no-, one-, and two-electron metal-metal bond. The  $2b_{3u}$  MO (LUMO for n = +2 and HOMO for n = 0, +1) was found to be largely composed of in-plane antibonding  $\sigma^*$ -type dimetal orbital

character as opposed to either out-of-plane  $\pi^*$ -type dimetal antibonding orbital character or bridging-ligand orbital character.

Extended Huckel MO calculations on the theoretical complexes  $\text{Ni}(\text{H}_2\text{C}=\text{CH}_2)_{2-4}$  and  $\text{Cr}(\text{H}_2\text{C}=\text{CH}_2)_6$  were carried out by Hoffmann and Rösch with geometry prediction as primary goal.<sup>347</sup> For example, maximized  $\pi$ -back donation requires  $D_{3h}$  tris(ethylene)nickel(0) to have all carbons and the Ni in one plane. The most symmetrical arrangement of 6 ethylenes about Cr, i.e., a structure of  $O_h$  symmetry, was predicted most stable for that molecule, with the steric effect determining stability here. Extensions to allyl systems were also presented. In an accompanying paper, Hoffmann, *et al.* constructs a molecular orbital model of MNO bonding schemes with particular attention being paid to interaction of the M fragment ( $\pi$ -donor or  $\pi$ -acceptor sites) with NO.<sup>348</sup> Another approach to deciphering the determining factor as to MNO bending considered the behavior of the  $[\text{MNO}]^n$  group ( $n$  = number of metal d electrons) in ligand fields.<sup>349</sup>

Ab initio calculations using the generalized valence bond method were carried out for the simple carbonyls,  $\text{TiCO}^+$  and  $\text{TiCO}$ , and discussion of the bonding in various states expanded to include  $\text{Cr}(\text{CO})_6$ .<sup>350</sup>

The complete electric dipole moment matrix  $eZ$  for (benzene)  $\text{Cr}(\text{CO})_3$  has been evaluated employing a multi- $\int$  atomic orbital basis on Cr, C, and O.<sup>351</sup> These results as well as those for a series of  $\text{h}^6\text{-RC}_6\text{H}_5\text{Cr}(\text{CO})_3$  molecules served to test various semi-empirical M.O. models in calculations of complete electric dipole moment matrices.<sup>352</sup>

The ligand field approach has been used to establish the probable ground state of chromocene ( $3d^4$ ) to be  ${}^3\Delta(\sigma\delta^3)$ ; Racah parameters B and C and the axial field quantities Ds and Dt were also evaluated.<sup>353</sup> In another application of ligand field theory, magnetic susceptibilities of  $d^x$  configurations in metal sandwich complexes were calculated.<sup>354</sup>

Miscellaneous studies, including measurements of thermodynamic quantities. Photodecomposition of gas phase transition metal ions such as  $\text{Cr}(\text{CO})_5^-$ ,  $\text{Cr}(\text{CO})_4^-$ ,  $\text{Fe}(\text{CO})_4^-$ ,  $\text{Co}(\text{CO})_4^-$ , etc., was monitored by the ion cyclotron resonance technique as a function of irradiation wavelength.<sup>355</sup> Assuming the ion disappearance mechanism is photodissociation, the spectra appear to reflect optical absorption peaks of the gas phase ions (ranging from 2-4 eV) which in turn are thought to arise from a charge transfer  $M \rightarrow L$  transition. The optical absorption peak energies as derived from threshold photodetachment curves vary directly with nuclear charge of M and the number of carbonyls in the anion.

Gas phase electron diffraction was used to determine the molecular structures of  $\text{Cp}_2\text{Cr}$  and  $\text{Cp}_2\text{Mg}$ .<sup>356</sup> A  $D_{5h}$  model was considered best for both molecules, with small ( $< 0.8$  kcal mol<sup>-1</sup>) barriers to internal rotation. The C-H bonds in  $\text{Cp}_2\text{Cr}$  were bent slightly out of the  $\text{C}_5$  plane and towards the Cr.

Heat capacities of  $\text{Cr}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  have been determined calorimetrically at 60-300°K and their enthalpies, entropies, and free energies were calculated.<sup>357</sup> The standard metal-CO bond dissociation entropies ( $\Delta\bar{S}^\circ$ ) are 35.1, 34.8, and 34.5 cal mole<sup>-1</sup> degree for  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$ , respectively. The products of the thermolysis of tungsten hexacarbonyl have been studied by other workers.<sup>358</sup>

The saturated vapor pressure of some chromium arene  $\pi$ -complexes has been determined by an effusion method.<sup>359</sup> Equations have been derived for correlating m.p., density, vapor pressure, and viscosity of bis(arene)metal derivatives (metal = Cr, Mo, W).<sup>360</sup>

The thermal decomposition of  $\text{Mo}(\text{CO})_6$  in a high-frequency field has led to a sharp increase in the rate of deposition of the metal at 20-400°.<sup>361</sup> A method has been developed for identifying the chemical form of stabilizing  $^{99}\text{Tc}^{\text{m}}$  after the  $^{99}\text{Mo}$   $\beta$ -decay from  $\text{Mo}(\text{CO})_6$ .<sup>362</sup>

Pulse photolysis studies of the Group VIb hexacarbonyls with oxygen and hydrogen have been carried out.<sup>363</sup>

Specific information regarding oxidation pathways was obtained in electrochemical investigations of  $\text{M}(\text{CO})_5\text{X}^-$  (M = Cr, Mo, W; X =  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ). The data was used to correlate known chemical oxidation and disproportionation processes.<sup>364</sup>

Acknowledgment. We are again this year most grateful for the expert help of Mrs. Helen George in putting together this Annual Survey.

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